MAR 8 1929

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 1 JULY, 1928 No. 1

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
1	Accelerated tests of organic protective coatings. Percy H. Walker and E. F. Hickson	1
2	Measurement of the tread movement of pneumatic tires and a discussion of the probable relation to tread wear. W. L. Holt and C. M. Cook	19
3	Absolute methods in reflectometry. H. J. McNicholas	29
4	Interferometer measurements of wave lengths in the vacuum arc spectra of titanium and other elements. C. C. Kiess	75
5	Analysis of bauxite and of refractories of high alumina content. G. E. F. Lundell and J. I. Hoffman	91

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
George K. Burgess, Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

July, 1928
Vol. 1, No. 1

PRICE, 25 CENTS
$2.75 PER YEAR ON SUBSCRIPTION
Sold only by the Superintendent of Documents, U. S. Government Printing Office
Washington, D. C.

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON
1928

Engin.
Inf. Doc.
3-8-29
amb.

ACCELERATED TESTS OF ORGANIC PROTECTIVE COATINGS

By Percy H. Walker and E. F. Hickson

ABSTRACT

This paper describes the equipment used at the Bureau of Standards in accelerated tests of paints, varnishes, lacquers, bitumens, etc.

A great variety of organic coatings, when subjected to a cycle of alternate exposure to light from an inclosed carbon arc, water spray and ozonized air, were shown to exhibit the same kind of decay as observed on exposure to the weather.

The difficulty of determining the relative condition of exposure tests is discussed, and methods for quantitatively determining when the coating ceases to protect are described.

CONTENTS

	Page
I. Introduction	1
II. Methods used to cause accelerated disintegration	2
1. Description of apparatus	2
2. Light source	2
3. Rain	4
4. Temperature changes (refrigeration)	4
5. Gases	4
6. Method of preparing test panels	5
7. Description of exposure cycle	5
III. Methods of determining extent to which disintegration has taken place	6
1. Observation by experts	6
2. Permeability to water vapor	9
3. Permeability to air	11
4. Electrical conductivity test	13
5. Use of milliammeter	14
6. Qualitative method for detecting pinholes, etc., in paints	15
IV. Summary	16

I. INTRODUCTION

The purpose of this paper is to describe the equipment in use at the Bureau of Standards for making accelerated tests of organic protective coatings, and to discuss the results obtained by its use.

The rapid testing of coatings to determine their probable relative durability under service conditions involves two distinct problems. It is necessary first to subject the coatings to conditions which will cause rapid deterioration of the character encountered in actual service. It is then necessary to determine the degree to which the

coatings have failed under the test conditions. The equipment now in use for subjecting test coatings to a variety of agencies which cause deterioration will first be described. Methods of determining the degree of deterioration will then be discussed.

II. METHODS USED TO CAUSE ACCELERATED DISINTEGRATION

Light, moisture, temperature changes, and varying small accidental additions to normal air are the important causes of decay of paint, varnish, and other organic protective coatings. In general, the most important of these is light.

1. DESCRIPTION OF APPARATUS

The chamber for exposure to light and moisture consists of a rotating cylinder made of No. 16 gauge galvanized iron, 76 cm (30 inches) in diameter, 38 cm (15 inches) high, open at both ends, with the light suspended in the center. This size was selected so as to bring the light as near the panels as possible, at the same time avoiding too high temperatures. The cylinder has a capacity of sixty 7.5 by 15 cm (3 by 6 inch) panels.

The test panels are placed in two tiers immediately opposite the light inside the cylinder, the panels thus being 38 cm (15 inches) from the center of the light source. This gives a temperature of about 52 to 55° C. at the panels with the type of lamp used. Thirty slotted holders, 7.5 cm (3 inches) wide and about 33 cm (13 inches) long for panels 7.5 cm (3 inches) wide, are attached to the inner surface of the open cylinder. The exposure cylinder is provided with water sprays, so that it is possible to expose the panels in succession to intense light and to a variety of moisture conditions. A pan placed about 5 cm below the bottom of the cylinder contains water and serves to keep the temperature down to about 52° C. next to the panels, as well as to humidify the air. Separate cabinets for exposure to gases and refrigeration are provided.

2. LIGHT SOURCE

In selecting a source of light it is advisable to choose a powerful light and one whose average intensity and spectral distribution will remain fairly constant. Whether or not the relative resistance to exposure of various coatings will be the same under sunlight as under a light of very different spectral distribution has never been determined, and until it is determined it seems desirable to use a light source as similar to sunlight as possible. Owing to absorption by the earth's atmosphere, no radiation of wave length shorter than 290 mμ reaches the earth.[1] The quartz-tube mercury-arc light which

[1] B. S. Sci. Paper No. 539, p. 592.

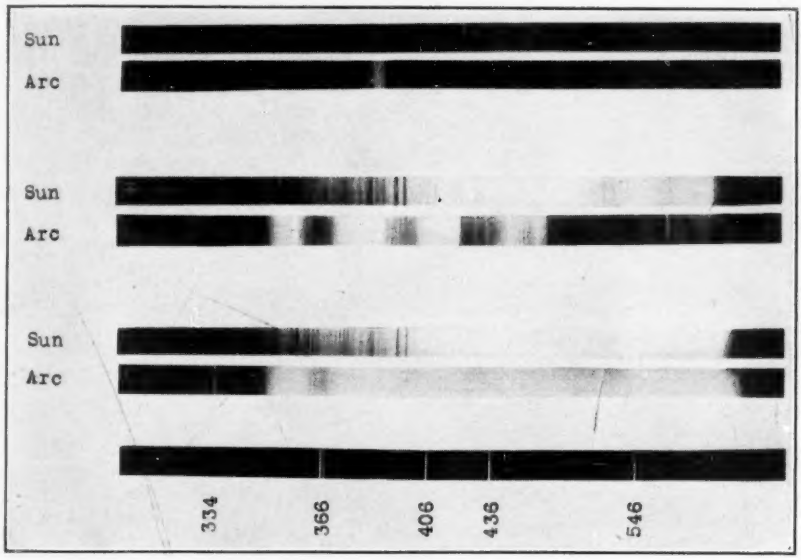

FIG. 1.—*Spectra of sun and of long-flame carbon arc, each at three different exposures*

The pairs of exposures are at comparable times. The numbers give the wave lengths in millimicrons of the mercury arc lines used for reference

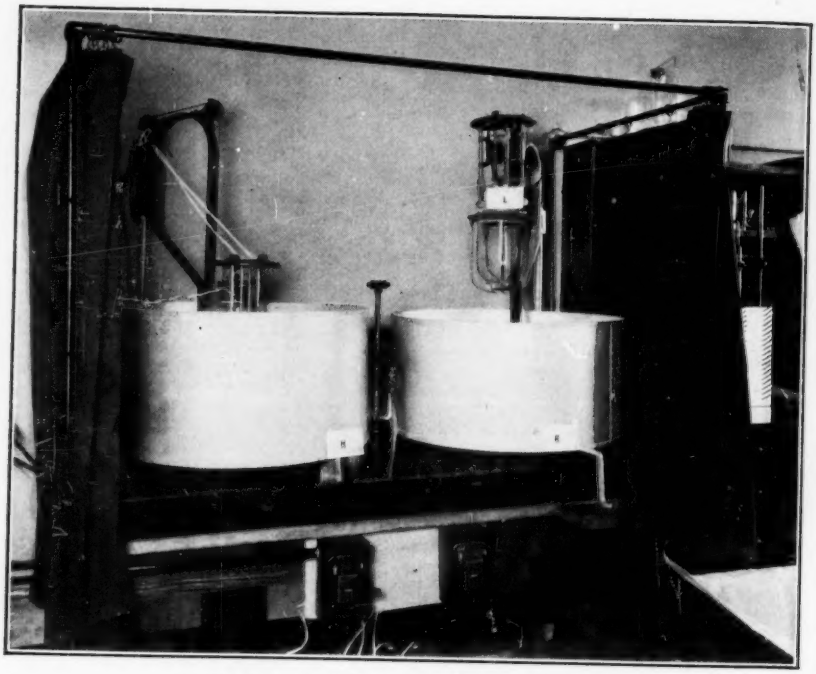

FIG. 2.—*Light exposure equipment*

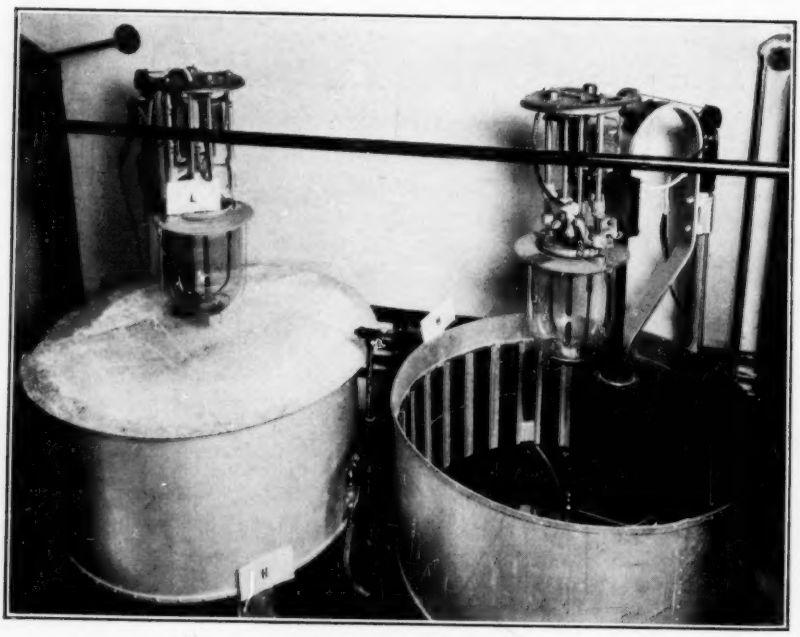

FIG. 3.—*Water spray (rain) equipment*

has been advocated by Nelson and others [2] has not been used as a source of light in this work. Most of the work recorded in this paper has been done with an inclosed type carbon-arc light operated at 220 volts d. c. at 13 amperes. Since the light is of the inclosed type the carbons can be operated with this current about 34 hours without renewal. The glass globe should be cleaned on each renewal of the electrodes.

Figure 1 shows (in comparison with sunlight) the spectrum of the arc used with the glass globe in position, taken on a panchromatic film in a quartz spectrograph. It is to be noted that the band spectra of both the arc and sun apparently become more continuous as the time of exposure is increased. Note also that while this arc spectrum shows much radiation in the moderate ultra-violet (350 to 400 mμ) it shows none of the very short waves not found in sunlight but given by the quartz mercury arc. The electrodes used are of solid carbon 12.7 mm in diameter. The glass globe is opaque to ultra-violet wave lengths less than 320 mμ and infra-red radiation longer than about 4,500 mμ. The total radiation at a distance of 38 cm (15 inches) from the center and at right angles to the arc on 12.6 amperes is 0.075 watt per cm^2. This is distributed in the spectrum as shown in Table 1.

TABLE 1.—*Spectral distribution of carbon-arc light with glass globe*

Spectral range	Per cent of the total radiation
320 to 360 mμ	2. 0
360 to 480 mμ	18. 5
480 to 600 mμ	9. 3
600 to 1,400 mμ	16. 5
1,400 to 4,200 mμ	22. 1
4,200 to 12,000 mμ	31. 6

The large amount of infra-red of wave lengths 4,200 to 12,000 mμ emanates principally from the glass globe which becomes heated by the arc, and is different in spectral composition from the infra-red from the incandescent arc. Owing to unsteadiness of the arc, which travels around the electrode, the radiation measurements varied by 20 per cent. A steadier arc would be obtained by operating at 20 amperes, but at this current the carbons would be consumed too rapidly.

Figure 2 shows two light units. In the left-hand unit the light is shown in position in the center of the cylindrical sample holder, *H*.

[2] Proc. Am. Soc. Test. Mtls., **22**, Pt. II, p. 485; 1922; Proc. Am. Soc. Test. Mtls., **24**, Pt. II, p. 920; 1924; Proc. Am. Soc. Test. Mtls. **26**, Pt. II, p. 563; 1926.

In the right-hand unit the light, *L*, is shown raised out of the cylindrical holder.

3. RAIN

In addition to light exposure, the panels should be subjected from time to time to several hours of vigorous spraying with warm (100° F.) water. The panels can be removed to a special chamber for this purpose, but it is more convenient to produce this artificial rain in the chamber used for the light exposure. For this purpose the light is raised out of the cylinder, a common rotating lawn sprinkler put in, the bottom of the bracket supporting the light is protected from spray by a brass cylinder and the top of the cylinder holding the samples covered by galvanized iron covers.

Figure 3 shows the arrangement for spraying the panels with water. The right-hand unit with the cover removed shows the rotating spray, the slots containing test panels, and the protecting tube over the lower part of the lamp support. The left-hand unit shows the lid in place.

In order to simulate a hot, humid climate a fixed water spray has been mounted in the tank in such a manner that it may function while the lights are operating. Connections for this spray are made at the tee above and between the two tanks. (See fig. 3.)

The light cylinders are also now made to rotate slowly, at the rate of three revolutions per hour. Thus with the lights in operation and in position (see fig. 2), a gentle spray can wet the test surfaces periodically while exposed to the light.

4. TEMPERATURE CHANGES (REFRIGERATION)

An ammonia coil about 27 by 47 by 40 cm in an insulated chamber that can be cooled to −25° C. (−13° F.) is used to quickly chill the test panels.

The test panels on removal from the light chamber are placed on the rack shown, and the rack with samples is placed in the refrigerator and left there for one hour and then removed.

5. GASES

It is most convenient to transfer the panels to a separate cabinet for exposure to various gas mixtures. Such a cabinet for exposure to ozonized air is shown in Figure 4. Air is forced, by means of the small motor-driven fan shown in the lower left corner, through a silica gel dehydrator, then through a calcium chloride bottle, which serves to indicate that the silica gel is working efficiently, to the ozonizing apparatus and thence to the glass chamber on the right for holding the panels. Some water is placed in the bottom of this

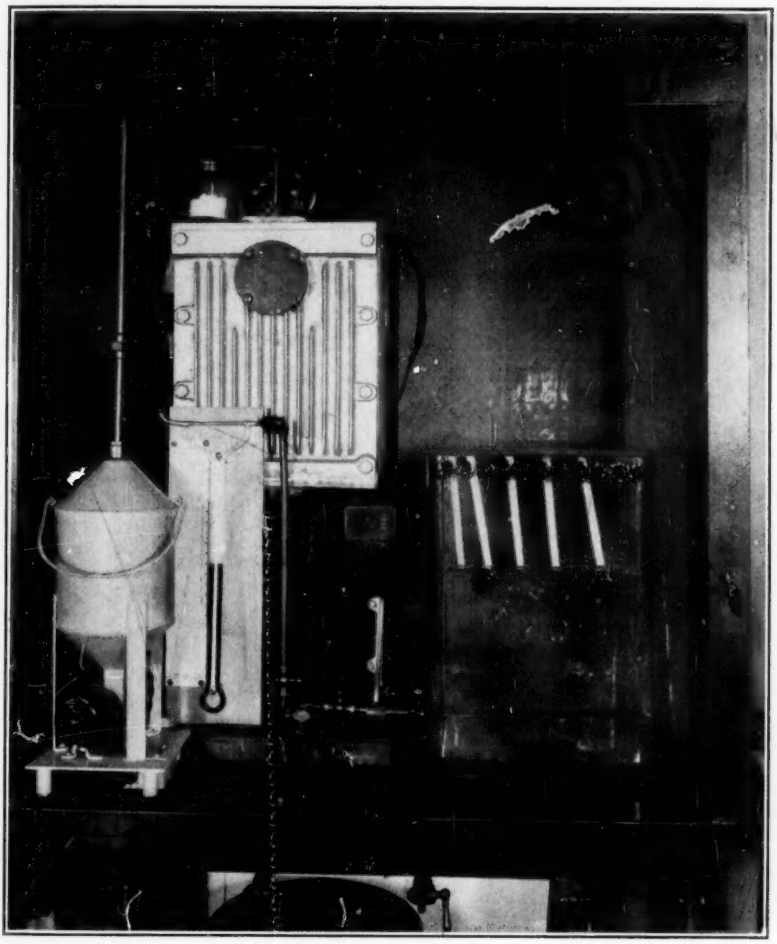

FIG. 4.—*Cabinet for exposing to ozonized air*

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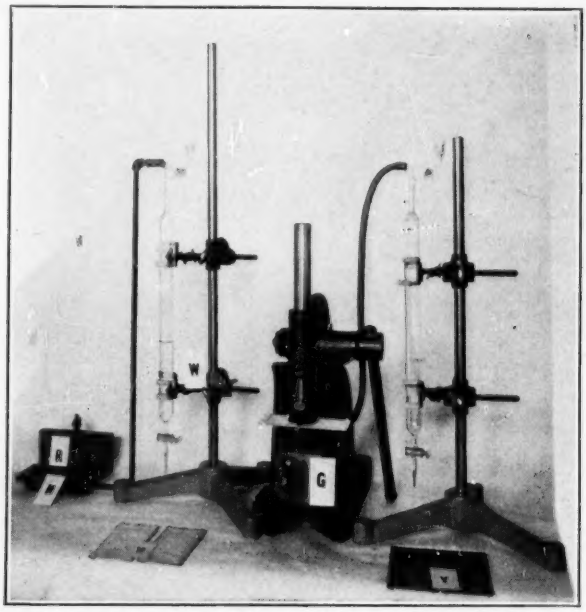

FIG. 5.—*Apparatus for determining breakdown of film by passing air through it*

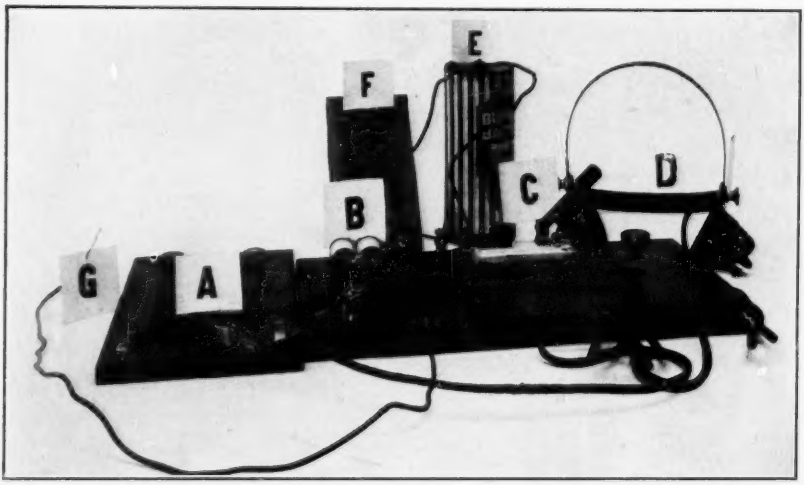

FIG. 6.—*Photograph and wiring diagram of Wilson's apparatus for determining end point of paint failures*

A, Steel wool contact frame. *B*, Buzzer. *C*, Switch. *D*, Head phones. *E*, Dry cell. *F*, Rubber stamp. *G*, Platinum tip

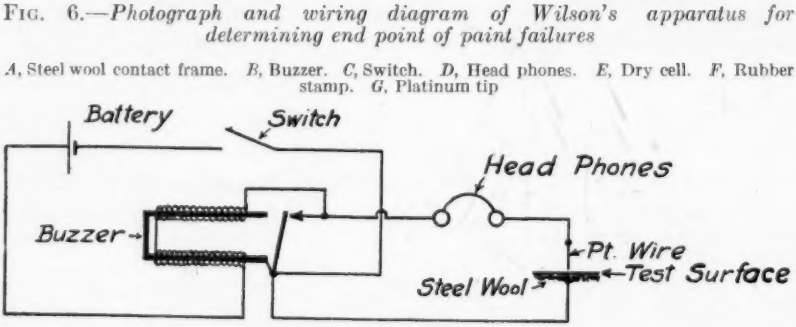

FIG. 7.—*Wiring diagram*

glass chamber to moisten the ozonized air. By suitable manipulation of the stopcocks in the pipe line the rate of flow can be determined by the flow meter, shown to the right of the silica gel holder, and samples for determining the ozone concentration can be taken through the pipe projecting toward the front. This equipment delivers about 660 liters per hour of air containing about 0.08 per cent of ozone by volume.

6. METHOD OF PREPARING TEST PANELS

It is a waste of time to make tests on single coats of protective coatings. This can be readily demonstrated by brushing and flowing paints on glass and, after drying, examining by transmitted light. It is advisable to always use at least two and generally three coats on the exposed test surface.

When using wood or metal, the back and edges of the panels are given three coats of aluminum paint (25 g of polished aluminum powder to 100 ml of long-oil water-resisting spar varnish). This aluminum paint is very waterproof and gives excellent protection to both wood and steel. Since, during exposure, it is not exposed to light it may be relied upon to last longer than any material being tested on the exposed surface.

In addition to tests on wood or metal, it is advisable to apply the material to 100-mesh wire gauze or to cotton cloth. This will be discussed later in connection with methods of determining the extent to which disintegration has taken place.

7. DESCRIPTION OF EXPOSURE CYCLE

Since light is the most important destructive agency in exposure tests, it seemed necessary to make use of as much light as possible. Therefore, the night hours (17 hours) were given over to light exposure. The idea in subjecting the panels to air containing a small amount (0.08 per cent) of ozone was to accelerate surface oxidation. In using refrigeration, the desired factor seemed to be a rapid change in temperature, rather than any definite time of exposure to the low temperature. The refrigerating unit was not assembled until some time after the light-exposure cylinder and gas chamber were made. In some of the earlier tests the panels were, therefore, not exposed to sudden temperature changes. The following tentative schedule shows the weathering cycle now in use:

Monday:

Ozonized air (wet atmosphere)	3½ hours (9.30 to 1).
Water (tap water at about 100° F., from a rotating spray)	3 hours (1 to 4).
Light (carbon arc)	17 hours (4 to 9).

Tuesday:	
Refrigeration (−10° F.)	1 hour (9.30 to 10.30).
Ozonized air	2½ hours (10.30 to 1).
Water	3 hours (1 to 4).
Light	17 hours (4 to 9).
Wednesday:	
Water	3 hours (9.30 to 12.30).
Refrigeration	1 hour (12.30 to 1.30).
Ozonized air	2½ hours (1.30 to 4).
Light	17 hours (4 to 9).
Thursday:	
Refrigeration (−10° F.)	1 hour (9.30 to 10.30).
Ozonized air	2½ hours (10.30 to 1).
Light	3 hours (1 to 4).
Water	17 hours (4 to 9).
Friday:	
Refrigeration (−10° F.)	1 hour (9.30 to 10.30).
Ozonized air	2½ hours (10.30 to 1).
Water	3 hours (1 to 4).
Light	17 hours (4 to 9).
Saturday:	
Ozonized air	3½ hours (9.30 to 1).
Water	3 hours (1 to 4).
Light	17 hours (4 to 9 Sunday).
Sunday:	
Light	24 hours (9 to 9 Monday).

Total operating hours=165 divided thus:	Hours	Per cent
Refrigeration	4	2.4
Ozonized air	17	10.3
Water	32	19.4
Light	112	67.9
Total	165	100.0

It will be noted that in this schedule only 165 out of 168 hours are accounted for. The remaining three hours are used for the inspection of the panels.

III. METHODS OF DETERMINING EXTENT TO WHICH DISINTEGRATION HAS TAKEN PLACE

1. OBSERVATION BY EXPERTS

Competent experienced observers frequently draw widely varying conclusions from inspection of the same panels, and the same observers draw varying conclusions at different times. This is well illustrated by the following:

One of the most carefully executed and widely known series of exposure tests was the Havre de Grace Bridge test of the American Society for Testing Materials. Nineteen paints designed as protective coatings for steel were used. Each of these paints was applied in three spreading rates—600, 900, and 1,200 square feet per

gallon. Triplicate panels were used for each spreading rate, making nine panels for each paint. The panels were exposed in November, 1906. The work was done with the utmost care and the various inspections were made by competent men experienced in such work. The divergent opinions of competent observers mentioned above are well illustrated in the following selection of 5 of these 19 paints.[3] The inspection was made May 5, 1910. The examination of the panels was divided into three heads, viz:

TABLE 2.—*Ratings of 5 out of 19 paints inspected May 5, 1910*

Paint	Examined for—	Aiken	MacNaughton	Tassin	Thompson	Hume	Average	Maximum	Minimum
2	A	8	9	[1] 1	8	9	8.5	9	1
	B	10	6	[1] 1	8	9	8.2	10	1
	C	6.44	6	[1] 1	4.33	4.66	5.3	6.44	1
10	A	8	9	10	6	9	8.4	10	6
	B	9	6	10	6	9	8.0	10	6
	C	10	9	10	8	9	9.2	10	8
11	A	9	9	10	6	7	8.2	10	6
	B	9	6	10	7.14	9.66	8.4	10	6
	C	10	8	10	7.14	9	8.8	10	7.14
13	A	8	10	10	8	9	9	10	8
	B	10	10	10	10	10	10	10	10
	C	8.55	7	10	6	9	8.1	10	6
14	A	9	9	10	8	8	8.8	10	8
	B	10	9	10	10	10	9.8	10	9
	C	10	8	10	6	9	8.6	10	6

[1] These values were not considered in computing the average of paint No. 2.

A. Chalking.
B. Checking, cracking, "alligatoring," etc.
C. General surface condition, with a marking for each as follows:
Excellent, 10 to 8.
Good, 8 to 6.
Fair, 6 to 4.
Poor, 4 to 2.
Failure, 2 to 0.

As far as possible members of the subcommittee were requested to pair off with such other members of Committee D–1 who were present though not of the subcommittee on inspection. Those of the subcommittee present were *W. A. Aiken, chairman, *G. W. Thompson, *M. MacNaughton, *A. P. Hume, Anderson Polk, A. H. Sabin, *Wirt Tassin. Those marked with an asterisk (*) sent in individual reports. A. H. Sabin was the only one who collaborated

[3] Taken from Proc. A. S. T. M., **10**, pp. 105–106; 1910.

with any other member of the subcommittee; he was with the chairman, who also was accompanied by Mr. Gibboney, of Committee D–1. The individual marks were averaged from all nine panels, covering three rates of spreading.

Another lot of 51 panels was inspected by a committee of seven members on April 15, 1910,[4] and by a committee of four on June 28, 1911.[5] Three of the four members of the 1911 committee were also members of the 1910 committee. In the 1910 ratings 18 panels had a maximum rating of 10 and only 6 of these a minimum rating as high as 8 and 8 had a minimum rating of 6 or less. Sixteen panels had a maximum rating of 9, with only 4 of these having a minimum rating of 8, and 8 having a minimum rating of 5 or less. The variation in the remaining 17 panels is proportionally as great, with the exception of 2 which were marked "0" by all members of the committee. Table 3 showing results on 7 of these panels was compiled from the two reports.

TABLE 3.—*Ratings of 7 out of 51 paints*

Paint No.	Date of inspection	W. H. Walker	P. H. Walker	Gardner	Chapman
7	Apr. 15, 1910	----------	9	8	8
	June 28, 1911	3	4	5	7
24	Apr. 15, 1910	----------	5	5	8
	June 28, 1911	5	7	2	8
333	Apr. 15, 1910	----------	7	9	9
	June 28, 1911	4	4	7	3
555	Apr. 15, 1910	----------	9	8	9
	June 28, 1911	9	9	6	9
777	Apr. 15, 1910	----------	9	8	9
	June 28, 1911	7	10	5	7
100	Apr. 15, 1910	----------	10	7	9
	June 28, 1911	5	8.5	4	8.5
5555	Apr. 15, 1910	----------	1	0	3
	June 28, 1911	4	8	2	7

Not only does this table show wide variation of opinion among competent observers examining the same panels, but it will be noted that all of the three observers who took part in both inspections rated one paint higher and one of the three rated two other paints higher in 1911 than in 1910.

These and other similar examples convince the writers that one of the greatest needs for the study of paint and similar coatings is

[4] A. S. T. M. Proceedings, **10**, p. 73; 1910. [5] A. S. T. M. Proceedings, **11**, p. 192; 1911.

method or methods for determining the time of breakdown of the coatings.

2. PERMEABILITY TO WATER VAPOR

Muckenfuss [6] more than 14 years ago suggested determining permeability to water as a measure of the breakdown of paint coatings and described preliminary experiments. Dunlap [7] has described a method used at the Forest Products Laboratory for determining the breakdown on weathering of paint on wood.

While using the same general idea of these investigations—determining the progressive change in permeability on weathering—the writers attacked the problem in different ways.

Twenty-three No. 100 [8] wire sieves 95 mm (3¾ inches) in diameter (71.26 cm^2 area) were given three coats as follows:

Sieves Nos. 1, 2, and 3, 8-gallon rosin-tung oil varnish.

Sieves Nos. 4, 5, and 6, 30-gallon rosin-tung oil varnish.

Sieves Nos. 7, 8, and 9, 50-gallon rosin-tung oil varnish.

Sieves Nos. 10, 11, and 12, the above 8-gallon varnish plus aluminum (2 pounds per gallon of varnish).

Sieves Nos. 13, 14, and 15, the above 30-gallon varnish plus aluminum (2 pounds per gallon of varnish).

Sieves Nos. 16, 17, and 18, the above 50-gallon varnish plus aluminum (2 pounds per gallon of varnish).

Sieves Nos. 19, 20, and 21, white lead-linseed oil paint.

Sieves Nos. 22 and 23, lead-zinc linseed-oil paint, B. S. Circular No. 89.

One week was allowed for drying between coats, and 1 week after applying the last coat the sieves were fastened by rubber bands to glass petri dishes containing dry $CaCl_2$, and then weighed. A blank consisting of a petri dish with dry $CaCl_2$, fastened with rubber bands to another petri dish, was also weighed. The samples, with the blank, were then put in air saturated with water for 20 hours, then conditioned for 1 hour at 30° C. and 32 per cent relative humidity and weighed again. This was repeated each day for 2 weeks. The average gains corrected for the blank were taken as the initial gains.

The coated sieves were then removed from the $CaCl_2$ dishes, exposed to the weather at 45° to the vertical facing south for a week, again fastened to the petri dishes over $CaCl_2$, exposed to saturated air for 20 hours, conditioned for 2 hours, weighed, the weight corrected for the blank, removed from the dishes and again exposed out of doors. A similar sieve uncoated and exposed to the same high

[6] J. Ind. and Eng. Chem., 5, p. 535; July, 1913.

[7] Ind. and Eng. Chem., 18, p. 1230; December, 1926.

[8] The openings in No. 100 wire sieve cloth are 0.149 mm; the diameter of the wire is 0.102 mm, and the area of the open space about 35 per cent of the total area.

humidity condition showed an average passage of about 7.4 g of water. The results are shown in Table 4.

TABLE 4.—*Permeability to water vapor of coatings on wire mesh exposed to weather*

Material (three coats)	8-gallon varnish	30-gallon varnish	50-gallon varnish	8-gallon varnish +Al	30-gallon varnish +Al	50-gallon varnish +Al	White lead-linseed oil paint	Lead-zinc paint F. S. B. Specification No. 10
Initial water absorbed through film ..... grams..	0.024	0.033	0.054	0.011	0.016	0.024	0.074	0.074
Less than 0.15 g water absorption through film after ..... weeks..	8	31	[1] 43	31	[1] 43	[1] 43	[1] 43	[1] 43
Less than 0.25 g water absorption through film after ..... weeks..	8	35	.....	[1] 43	.....	.....	.....	.....
Less than 0.50 g water absorption through film after ..... weeks..	8	39	.....	.....	.....	.....	.....	.....
Less than 1.00 g water absorption through film after ..... weeks..	8	[1] 43	.....	.....	.....	.....	.....	.....
Less than 1.50 g water absorption through film after ..... weeks..	10	.....	.....	.....	.....	.....	.....	.....
Less than 2.00 g water absorption through film after ..... weeks..	11	.....	.....	.....	.....	.....	.....	.....
Less than 2.50 g water absorption through film after ..... weeks..	12	.....	.....	.....	.....	.....	.....	.....
Less than 3.00 g water absorption through film after ..... weeks..	12	.....	.....	.....	.....	.....	.....	.....
More than 3.00 g water absorption through film after ..... weeks..	13	.....	.....	.....	.....	.....	.....	.....

[1] More than.

TABLE 5.—*Permeability to moisture—accelerated cycle*

Paint	Water absorbed by calcium chloride through coatings (grams)			
	Before exposure	After exposure to accelerated cycle		
		41 days	48 days	55 days
White lead and linseed oil	0.03	0.06	0.07	0.08
	.03	.06	.09	.06
Lithopone and linseed oil	.03	.12	.20	.41
	.03	.11	.25	.48

The early stages of the above investigation were so encouraging that two paints were tested in a somewhat similar manner in the accelerated cycle (without refrigeration). For this test rectangular brass frames 7.5 by 15 cm to hold the No. 100 sieve cloth were prepared and three coats of the paint applied as before. Permeability was determined by clamping a glass weighing tube containing $CaCl_2$ to the cloth, using rubber washers to make tight joints. The results are shown in Table 5. Here again the results are what experience with these paints would indicate.

3. PERMEABILITY TO AIR

This work on sieve cloth was so encouraging that a number of similar panels were prepared, coated with various well-known paints, and subjected to the accelerated cycle. It was soon found, however, that the experimental errors were so large, owing to the small amount of water taken up and the difficulty of learning whether the joint between the film and the weighing tube was tight, that it was decided to abandon the gravimetric method and to use a method of measuring the air passing through the film under definite conditions. Apparatus for this had to be designed and made, and this took so much time that the exposure to the accelerated cycle had in many cases gone too far before any measurements were made.

Figure 5 is a photograph which shows the apparatus finally developed. *Y* shows unpainted and painted wire sieve cloth in brass frames; *N* and *R* show bottom and top of a cell for holding the whole frame and to the left of *G* a similar cell for clamping a portion of the painted gauze. Rubber gaskets on top and bottom of the gauze panels serve to make an air-tight connection when the cell is compressed in the arbor press *G*. The lower compartment in the cell is joined by an air-tight connection to one of the large burettes shown to the right of *G* and the left of *W*. The water is adjusted to a mark in the upper constricted portion and with the cock in the upper portion of the cell closed the burette cock is opened. When water does not fall in two minutes below a zero mark on the burette (previously determined), the joint is considered tight. The cock in the upper part of the cell is then opened, the burette read after two minutes, and the volume recorded. The small cell has the disadvantage that at each test the painted gauze is compressed between rubber gaskets, and the advantage that three readings can be made on each panel. The large cell, *R* and *N* (which on account of the difference in volume gives a different zero point on the burette), with the bolted type of frame shown in the figure, is very difficult to make tight. With frames soldered on the edges instead of bolted, tight joints can be made with this cell. It has the advantage of not compressing the test film and the disadvantage of giving only one reading on each panel.

Since all of the paints were applied to the bolted panels, the small cell was used, and three readings were taken on each panel or six on each paint.

The exposures to the accelerated cycle were started July 19, 1927. After one month panels 7 and 8 (lithopone linseed-oil paint) showed such complete disintegration by visual inspection that they were

removed from the test and kept in a clean, dry container. The remaining panels were subjected to the accelerated cycle for four months. The permeability tests were made November 21, 1927. The results are shown in Table 6.

TABLE 6.—*Permeability of various paints after four months in accelerated cycle*

Panel No.	Paint exposed July 19, 1927	Average permeability (ml air in 2 minutes) on Nov. 21, 1927
5 and 6	Basic carbonate white lead and linseed oil	118.5
7 and 8 [1]	Lithopone and linseed oil	122.5
9 and 10	5 and 6 paint + lampblack	76
11 and 12	Red lead and linseed oil	119.5
15 and 16	Black linseed oil paint, F. S. B. specification No. 14b	1.5
17 and 18	Red enamel, F. S. B. specification No. 19b	1.5
19 and 20	Titanium zinc paint, F. S. B. specification No. 278	16
21 and 22	19 and 20 paint + lampblack	38
23 and 24	Green linseed oil paint, F. S. B. specification No. 15	25.5
25 and 26	Lead-zinc linseed oil paint, F. S. B. specification No. 10b	11
27 and 28	25 and 26 paint + lampblack	13
	Unpainted No. 100 sieve cloth	132

[1] These panels were exposed exactly 1 month and then discontinued, because under the microscope the coating was cracked all over. They were by far worse than any other panels.

In general, these results confirm the other experiments in indicating that the method is valuable. The lithopone paint which shows up worst in the test is known to be a paint of poor durability. Black linseed oil paint is known to be one of the most durable paints. The red enamel, which is the only paint equaling the black in this test, is also a very durable paint. The slightly better showing of the untinted titanium zinc and lead zinc paints as compared with the same paints tinted is not what would be expected. It is possible that longer exposure may show different results with these; for this reason these discrepancies are not considered of any moment. The decided breakdown of red lead as compared with two of the white paints suggests that the supporting surface may influence the results. It is possible that bronze wire screen has some deleterious effect on red lead-linseed oil paint. It is clear that more work must be done with this method of determining the end point of paint failures before a positive opinion as to its real value can be expressed. However, the results as a whole are encouraging, and we expect to repeat some of the work in Table 6, and since the nature of the wire gauze may influence the behavior of some paints it is proposed to apply paints to cotton cloth as well as to wire gauze.

4. ELECTRICAL CONDUCTIVITY TEST

On August 31, 1927, Doctor Liebrich and Doctor Kerscka, of the Chemisch-Technische Reichsanstalt, Berlin, showed one of the writers a simple apparatus for testing the continuity of an insulating film on metal. A telephone receiver is connected with the back (unpainted) side of the steel panel. A voltage from an interrupted source is placed across the receiver, and the return wire ending with a fine metal brush is drawn across the painted surface. Breaks in the paint surface are indicated by a buzz in the telephone.

J. H. Wilson, assistant chemist in this laboratory, has investigated this method. He found that the simple brush used by Liebrich and Kerscka would detect rather large uncovered areas but would not detect many of the visible cracks. Wilson has, however, modified the method by placing drops of a conducting liquid that will readily wet the coating on the painted surface and completing the circuit by dipping the end of the wire in these drops. The test panel, after some of the paint is scraped from the back side, is laid on a frame of metal wool, which is connected with one lead from the battery, and evenly spotted with the conducting liquid with the rubber stamp (*F* in fig. 6). After about two minutes the platinum tip of the other lead is inserted in each of the drops. Since there are 50 drops, the number of buzzes multiplied by two gives the percentage of breakdown.

Ten commercial samples of olive green automobile enamels (oleoresinous type) were tested on 7.5 by 15 cm black iron panels. Three coats, allowing one week between coats, were applied to all panels, four panels being prepared with each sample. Two of these four panels were subjected to the accelerated cycle (without refrigeration) and two were exposed outdoors 45° to the vertical, facing south. The exposures were started in March, 1927. The accelerated tests were rated by inspection after 10 days. The outdoor tests were rated by inspection after one month. The accelerated tests were then continued for a total of 35 days and the outdoor tests for 146. After 35 days' accelerated testing each panel showed by inspection greater deterioration than the corresponding 146-day outdoor panel.

They were then tested using Wilson's method. A summary of the results is given in Table 7.

TABLE 7.—*Tests of olive green oleoresinous automobile enamels*

No.	Composite rating on loss of gloss, discoloration, chalking, and cracking after 10 days' accelerated test	Rating on cracking alone after 10 days' accelerated test. In the columns marked on scale of 10, 1 being best	Rating after one month outdoor exposure	Rating by Wilson's test, per cent destruction	
				Accelerated panels after 35 days' accelerated test and storing in clean, dry compartment	Outdoor panels after 146 days' exposure and storing in clean dry compartment
1	A	1	No change	20	2
2	B	1½	Film whitened	12	2
3	A	1	No change	34	2
4	C	7	Checked all over	100	92
5	A	1	No change	14	2
6	B	6	do	52	6
7	A	4	do	14	0
8	C	9	Checked all over	100	58
9	C	9	do	100	32
10	A	1	No change	40	2

A=One of five best.
B=Intermediate.
C=One of three worst.

This test and similar results obtained with various bituminous materials on aluminum indicate that this method is very useful for recording the failure of protective coatings on metal. The method is rapid and, with proper care, quite easy of execution. It is important, however, to select a suitable wetting liquid. For glossy, hard coatings that have a tendency to repel water a dilute (0.5 per cent) soap solution is generally suitable. On chalky, soft films this solution spreads so rapidly that the individual drops flow together before the contacts can be made. For such coatings a dilute (0.5 per cent) solution of sodium chloride is generally suitable.

This test can be applied to almost all organic coatings for steel. Aluminum paint, however, has been found to be a sufficiently good conductor to give a buzz even when there is no break in the film. Other such coatings may be found, hence one should make sure that the undamaged coating does not cause a buzz before using this test. As may be expected, the intensity of the buzz given by the different drops varies greatly. However, the method gave good results.

5. USE OF MILLIAMMETER

It seemed desirable to the authors to obtain some quantitative measure of the current passing through various sections of the paint coatings. With valuable assistance from C. M. Saeger, jr., the following methods were used: A milliammeter, having a scale reading from 0 to 60 milliamperes, was connected in series with a battery and the test specimen. The current was adjusted with a resistance

so that a bare metal panel gave a reading of nearly 60 on the scale. Freshly painted panels gave readings of zero. Exposed panels that were still in good condition gave readings of 2 or 3 milliamperes, while badly cracked coatings gave readings as high as 50 milliamperes. It was decided to reduce the total number of spots to be tested from 50 to 12, but to increase the diameter of the spots from approximately 8 to 12.2 mm (0.5 inch). These spots were equally distributed over a test area measuring 5 by 12.7 cm (2 by 5 inches). Previously some trouble was caused by the electrolyte disappearing after being stamped on the panel. This took place particularly on chalky, porous coatings. To overcome this trouble, a measured volume (about 0.1 ml) of the electrolyte was applied to a test area, and after one minute a reading was taken before applying the electrolyte to the next area. This method gave good results.

In order, however, to keep the diameter of the wetted spot exactly the same in all cases, it was finally decided to use a porous or spongy material in contact with the specimen during the test. A satisfactory material was a mixture of silica sand (free from clay) and rubber cement. This was molded into a cylinder 12.2 mm (0.5 inch) in diameter by 76.2 mm (3 inches) long. A copper terminal was embedded in this electrode. This was placed in a small glass cell containing the electrolyte. The electrode was found to have excellent capillary attraction. In making a test the painted side of the specimen was placed on top of the electrode for one minute before applying the current from the battery. This method of applying the electrolyte gave wetted spots having the same diameter and proved satisfactory. No trouble was experienced in obtaining readings that could be checked. It is possible to have either a single electrode and test the specimen in definite positions or to have a number of electrodes (about 12) in a fixed position and set the specimen on these. The condition of the battery and the electrical connections can be checked by noting the milliammeter reading on a standard bare plate before and at the end of a test. After finishing with the test specimens they were rinsed with clean water and returned to the exposure cycle.

6. QUALITATIVE METHOD FOR DETECTING PINHOLES, ETC., IN PAINT COATINGS

The usual practice in preparing paint panels for exposure tests is to apply several coatings and then assume that the panel is completely covered. It seemed desirable to apply some simple and rapid test to the coated area to prove that the metal was entirely coated.

The improved ferroxyl test of Pitschner [9] for detecting the porosity of electroplated coatings on ferrous metals was first tried on electroplated articles with excellent results. In attempting to adapt this test to paint coatings, it was found that the "ferroxyl" reagent on the paper was apparently repelled by the paint coatings. This possibly could be corrected by experimenting, but no further work was done with the method. The idea of Pitschner of using coated paper for his studies on electroplated material led the authors to try various methods for obtaining results. The following method was found rapid and satisfactory. Sheets of filter paper, or any good grade of unsized bond paper, are cut into proper sizes for the test panels 7.5 by 15 cm. In applying the test, one of the sheets is immersed in a weak (0.5 per cent) sodium chloride solution containing a few drops of phenolphthalein indicator (0.1 per cent alcoholic solution). The paper, moistened on both sides, is spread over the coated specimen, avoiding air pockets. Connection with a dry cell is made to the bottom of the plate and an electrode from the negative pole passed across the wetted paper. Within a few seconds, an intense red shows on the white paper if any bare metal is present. Pinholes, etc., can be accurately located. Invariably it was found that the edges of freshly painted panels gave a fine red line the length of the panel. It is well known that the edges of metal panels are generally the first parts to show corrosion. Cracks on weathered panels are readily located by the method. The print, likewise, gives a good quantitative idea of the number and size of the cracks. After the test the panels are washed in clean water and allowed to dry.

It is intended that these quantitative methods should supplement the usual practice of visual inspection of the appearance of the coatings, including such important properties as change in color, loss of gloss, surface checks, wrinkles, etc.

IV. SUMMARY

Apparatus for exposing organic protective coatings to artificial light, water, and gases is described.

A variety of materials, including varnishes, oil paints, enamel paints, lacquers, bituminous saturated felts, bituminous roofing materials, have been tested in a proposed accelerated cycle. As judged by visual inspection the nature of the breakdown is remarkably similar to the breakdown of the various materials on weathering. There is chalking with paints that chalk in service, cracking with those that crack, and similar changes in color. The characteristic differences in behavior of various asphaltic mixtures observed on outdoor weathering are duplicated in the accelerated cycle. The same may

[9] Karl Pitschner, "A rapid and practical method of applying the ferroxyl test to protective coatings," Proc. Am. Soc. Test. Mtls., **27**, Pt. II, p. 304; 1927.

be said of varnishes and lacquers. In fact, the duplication of weather effects has been remarkable with all types of materials tested.

While failure in the accelerated cycle is similar to and more rapid than that on weather exposure, no definite ratio has as yet been fixed between the accelerated test and weather test. This is readily evident from a consideration of the variations in the weather.

The difficulty of determining the relative condition of protective coatings is discussed, and the unreliability of opinions based on visual inspection is pointed out. Several methods of quantitatively measuring the extent of failure of such coatings are described. These include measuring the amount of water vapor under definite conditions or amount of air under definite pressure passing through coating on wire gauze and several plans of locating and measuring breaks in a coating on metal by electrical means.

The writers gratefully acknowledge the work of B. H. Carroll in photographing the comparative spectra shown in Figure 1, and of W. W. Coblentz in determining the total radiation and spectral distribution given in Table 1.

WASHINGTON, February 25, 1928.

MEASUREMENT OF THE TREAD MOVEMENT OF PNEUMATIC TIRES AND A DISCUSSION OF THE PROBABLE RELATION TO TREAD WEAR

By W. L. Holt and C. M. Cook

ABSTRACT

From an observation of the ways in which pneumatic-tire treads wear in service, it appears that the movement of the tread when in contact with the road is probably an important cause of wear. In this paper two methods are described for recording tread movements as a tire rolls along under load. One way, which is referred to as the wax-plate method, is particularly adapted to this work because the tread movements can be recorded quickly and easily with very simple equipment. The results of several tests by this method are shown, and some of the factors in tire construction and operation which affect tread movements are determined. Methods for the reduction of this tread movement are suggested which should have a direct bearing on the reduction of tread wear.

CONTENTS

		Page
I.	Introduction	19
II.	Methods tried	20
III.	Results with different tires	21
IV.	Influence of different factors on the tread movements	23
V.	Discussion of results	25
VI.	Conclusions	28

I. INTRODUCTION

In this investigation a study of the manner in which pneumatic-tire treads wear has been made by observing the movement of the tread when in contact with a flat surface. The matter of tread wear has come very much to the front since the general adoption of the balloon tire, which, because of its greater deflection and larger tread contact area, presents a more serious problem in this respect than the high-pressure tire. The thought which is being given to this problem is illustrated by the many references to "flat treads," "round treads," "center hinges," "riding strips," etc. Under normal conditions a tire should be expected to wear uniformly and symmetrically around its periphery, but it is a matter of general observation that

treads do not always wear in this way. Some of the common ways of wearing nonuniformly are "cupping" of treads on each side of the center line, wearing of the edges of the buttons, and nonsymmetrical wear with respect to the center line of the tire. Accordingly, it was felt that a study of the way in which treads are abraded should yield valuable information concerning the causes of tread wear, and thus indicate the most economical use of rubber in the tread.

II. METHODS TRIED

Tread movements were observed and recorded by several different methods.

One method made use of a revolving slotted disk driven by an electric motor, the speed of which could be controlled. A tire was mounted on an ordinary type of test machine in which the tire revolves against a metal drum. By mounting the revolving disk close to the contact surface of the tire and the drum and adjusting the speeds properly the tread movement just before coming in contact with the drum could be observed. However, it was not possible to obtain data as to what occurred after the tire came in contact with the drum.

Another method tried was to coat the tire tread with a white enamel sufficiently flexible so that it would not chip. The tire was run for a short time against an abrasive surface with the thought that movements of the tread would show up by corresponding scratches on the enamel. The results of a trial, however, did not look promising and the plan was abandoned.

The next experiment was made with an apparatus by which a tire could be pressed against and rolled along a heavy glass plate, through which the tread movement could be observed. This apparatus is shown in Figure 1. The tire is mounted on the shaft of the motor simply for convenience, as the motor itself is not used. A loading device permits the tire to be pressed against the plate glass, which is secured to a small carriage. The carriage can be moved up and down by turning the handle which operates through a rack and pinion. Thus the action of a tire in rolling along a flat surface is simulated. The glass plate is ruled and etched in 1-inch squares as reference lines. It would probably be desirable to subdivide these into one-tenth inch over at least the central portion of the glass. By noting successive positions of any particular point on the tire with respect to a reference point on the glass the movement of the tread rubber can be studied. In order to show up the area in contact plainly it is advisable to coat the glass with a liquid, such as a soap solution or glycerin. If desired, photographs can be taken through this glass as the tire rolls. (See fig. 2.) Visual observations, however, may furnish

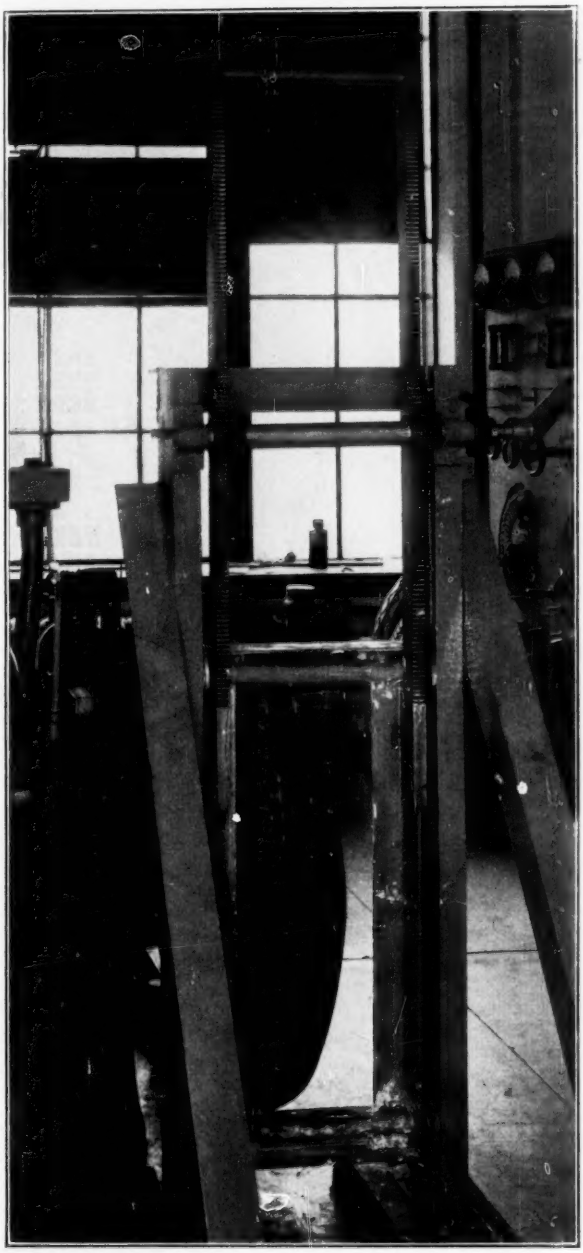

FIG. 1.—*Apparatus used for observing tread movements through a glass plate*

FIG. 2.—*Photograph taken through the plate glass showing the contact area of a tire under load*

(The depressions in the tread were painted white to show contrast)

all the information that is desired. In obtaining data which could be plotted as graphs, a telescope was mounted about 6 feet away, and observations made through it. This aided considerably in following the movement of particular points in the tread.

Observations of several tires showed that different parts of the tread had characteristic movements. For instance, the central part of a tire usually showed straight-line movements opposite to the direction of travel of the tire, while other parts had a curved movement with a component of motion in the same direction as that in which the tire traveled.

Plotting tread movements in this way, however, is a rather tedious process; therefore, a quicker method was tried which proved to be very satisfactory for recording the complete movement of any point on the tread. This method consists of recording the movement on waxed plates and is carried out as follows: Aluminum sheets about 8 by 10 inches and 0.010 inch thick are given a thin coating of melted paraffin wax on one side. Several different waxes were tried out, but paraffin was found to give the best results at ordinary room temperature. Harder waxes were not satisfactory. After the wax has set, the surface is sprinkled very sparingly with grains of No. 60 carborundum. As a tire under load flexes when rolled over one of these plates, the carborundum grains (or at least a portion of them) stick to the tire and trace their path on the waxed plate. It is well to roughen the surface of the tread slightly (as with sand or emery paper) to remove any glaze, and give a better chance for the grains to stick.

Figure 3 shows photographs taken of a typical wax-plate record. The straight lines in the central part of the treads and the more or less curved lines in other parts were traced by the individual grains of carborundum.

Records were made from several tires by using the apparatus shown in Figure 1, and interposing the waxed plates between the tire and the glass. However, it was found that practically the same records could be obtained by using an ordinary drum tire testing machine and allowing the waxed plates to pass between the tire and the drum. This offered several advantages because in addition to being more convenient it permitted records to be made under normal conditions of speed and tractive effort.

III. RESULTS WITH DIFFERENT TIRES

Different tires were mounted on a drum test machine [1] and records made of the tread movements under air pressures and axle loads corresponding to normal operating conditions. The tire was turned by hand at a speed corresponding to about 2 miles per hour as the waxed plate passed between the tire and the drum. From these

[1] The dynamometers which are described in B. S. Tech. Paper No. 213, Power Losses in Tires, were used.

records, the line drawings shown in Figure 4 were made. The arc above each section shows the profile of the raised portion of the tread. These are not intended to be absolute reproductions of tread designs or tread movement, but rather to show what may be expected from different tires and the approximate movements of points in the tread.

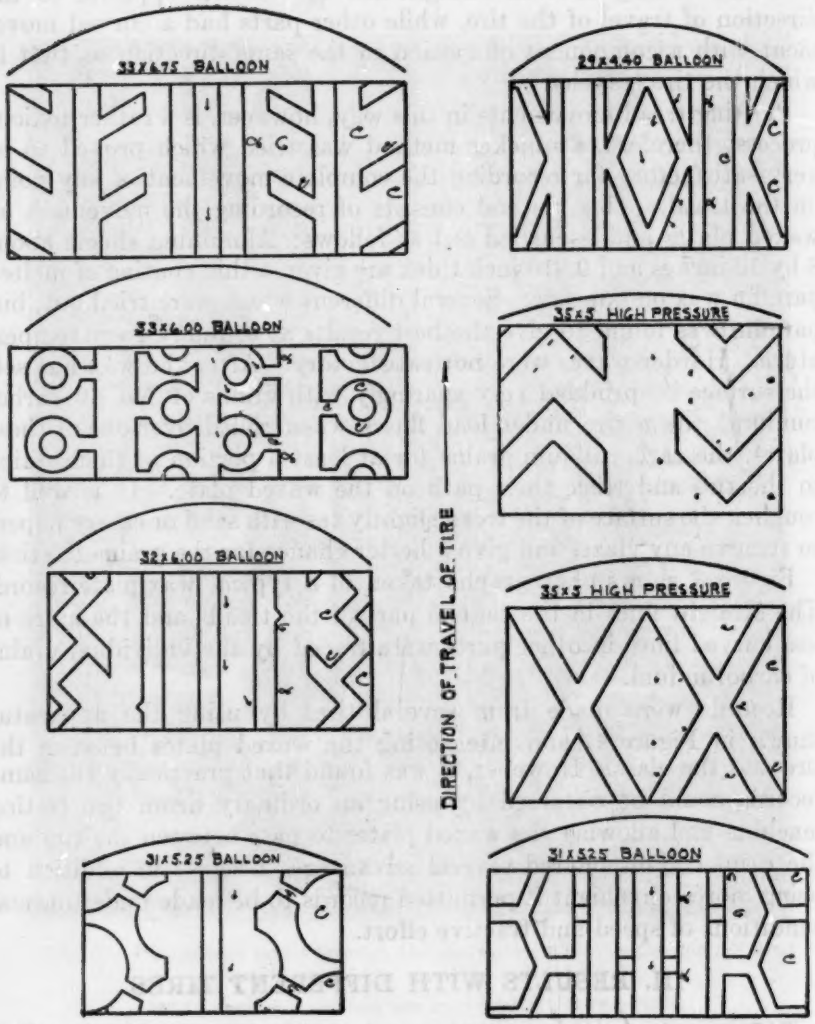

FIG. 4.—*Drawings taken from wax records showing tread movements of different tire treads*

It will be noted that the general movements in all the treads are similar. Each tread may be divided into three parts—the center, the intermediate portion, and the outer portion. In the center of the tread the movement is in an approximate straight line along the

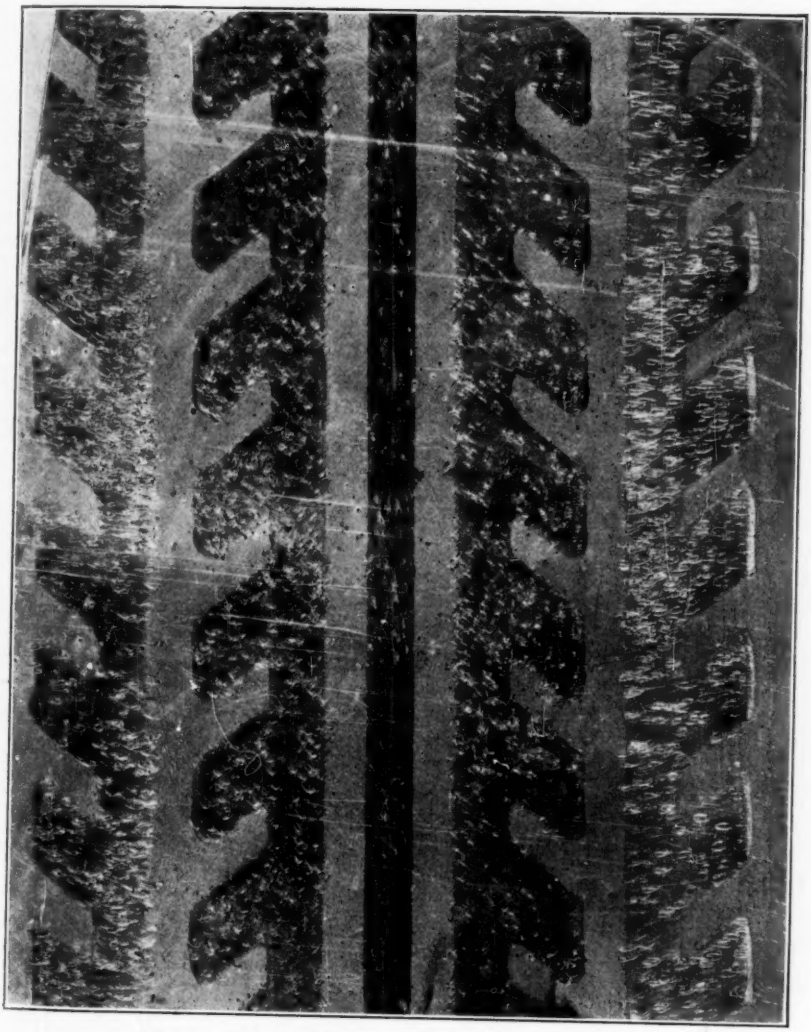

FIG. 3.—*Typical wax plate showing tread movements*

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circumference in a direction opposite to the direction in which the tire travels. The outer portions of the tread also have circumferential movements, but in the direction of travel. In addition, they move toward and away from the center line, thus giving the curves observed. The intermediate portions move similarly, but the resultant movement may be either in the direction of travel or against it, depending largely on the distance from the center line. A V-shaped mark on a wax plate is a common record from this part of the tread.

IV. INFLUENCE OF DIFFERENT FACTORS ON THE TREAD MOVEMENTS

The question is apt to arise as to whether the results made by simple rolling tests at very low speeds are comparable with those obtained at higher speeds. As noted previously, the method of recording on waxed plates permits of records being made at a considerable tire speed. Records were made on tires running at speeds as high as 30 miles per hour. The waxed plate was simply dropped between the tire and the drum and allowed to fall on the floor after passing through. The treatment was a little severe, but in most cases the wax record was not damaged. The results seemed to be entirely comparable with those obtained from the same tire at very low speeds.

Some records were also made using a tire running at a speed of 22 miles per hour while transmitting 0, 4, and 8 horsepower, respectively, corresponding to tractive efforts of approximately 0, 70, and 140 pounds. The results are illustrated in Figure 5.

The scratches in the center of the tread are increased in length as the tractive effort is increased, which is in accordance with what is to be expected. The circumferential movement of points in the intermediate portions of the tread are increased while circumferential movements of the outer portions (which are normally in the direction of travel) are decreased. The large movement, however, toward and away from the center does not appear to change appreciably with a change in tractive effort. A large tractive effort, such as might be produced by a sudden application of the brakes of an automobile or very rapid acceleration, would be outside the scope of this study.

The air pressure and the axle load under which a tire is operated affect the tread movement considerably. The greatest tread movements occur under low air pressures or high-axle loads. The movement, however, appears as simply an exaggeration of that which occurs under normal operating conditions and increases with increased flexing. Figure 4 shows both high pressure and balloon tires. The movement is more pronounced in the balloon tire, which is in accord-

ance with the common observation that the treads of balloon tires are inclined to wear faster and less uniformly than the treads of high-pressure tires.

The common practice of cambering and toeing in of the front wheels of an automobile doubtless influences the tread wear. It

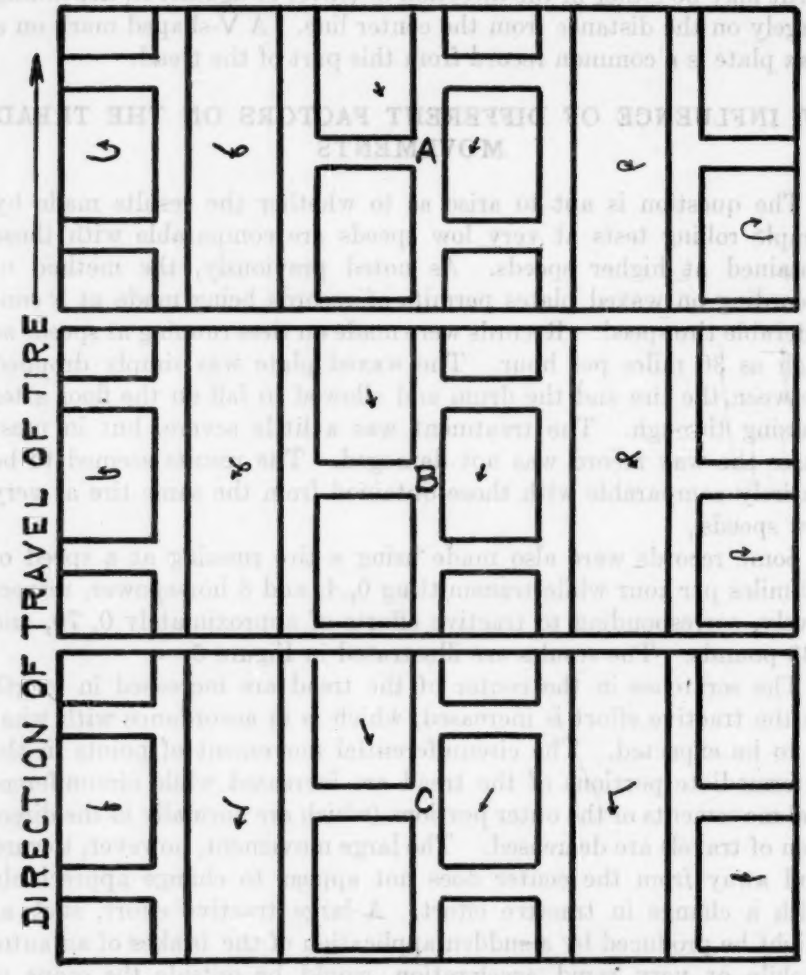

FIG. 5.—*Drawings taken from wax records showing the effect of tractive effort on tread movements*

A.—No tractive effort.
B.—70 pounds tractive effort.
C.—140 pounds tractive effort.

should not be difficult to determine the effect of these factors on the tread movements either in the laboratory or on the road by the use of waxed plates.

The results of these tests indicate that the movement of a tread may be affected by the direction of rotation, particularly in the case

of a nonsymmetrical design. It was noted that with some tires the tread movement is excessive at certain points, particularly at the ends or edges of nonskid buttons. From an observation of the way in which a button comes in contact with and leaves the ground, it would seem desirable to design the buttons so that the edges would be approximately parallel to the periphery of the area of tire contact. This would tend to make the total button come into contact quickly after once touching.

Aside from indicating some of the causes of tread wear, this study points to the desirability of occasionally changing the direction of rotation of tires in service.

There has been a tendency recently to make tire treads in which the design is comparatively open in the center and which have more or less continuous "riding strips" some distance out from the center. An attempt was made to obtain data on the change in tread movements due to increasing or decreasing what might be called the rigidity of the center of the tire. The results are illustrated in Figure 6. Four different degrees of rigidity are shown which were produced either by cutting additional depressions in the tread or by filling some of the depressions of the original design with strips of rubber. This naturally did not give as rigid a condition as would result from a homogeneous mass, but should approximate this condition. *A* shows the most flexible tread condition while *D* shows the most rigid condition. The movements of the intermediate and outer portions of the treads shown in *A*, *B*, and *C* seem about the same. The center movements are somewhat erratic. In *A* the center movement apparently depends on whether or not a button as a whole is distorted without slipping. In *B* there seems to be an increased tendency to crowd toward the center depression. In *C*, on account of the increased rigidity in a circumferential direction, there seems to be a tendency to crowd away from the center. In *D*, the movement of the whole central portions is less than in the other cases, but the outside movement is increased.

In Technologic Paper No. 240 (Dynamometer Tests of Automobile Tires) it was shown that the creep of a tire is dependent on the carcass design as well as on the tread design. This indicates that the tread movement is affected by the carcass as well as by the tread configurations.

V. DISCUSSION OF RESULTS

The results obtained by recording the tread movements indicate that at least a considerable part of tread wear may be caused by the slipping of portions of the tread over the road surface in changing from the normal to the deflected condition and vice versa. This might be termed a scuffing action. It is recognized that a tire seldom rolls

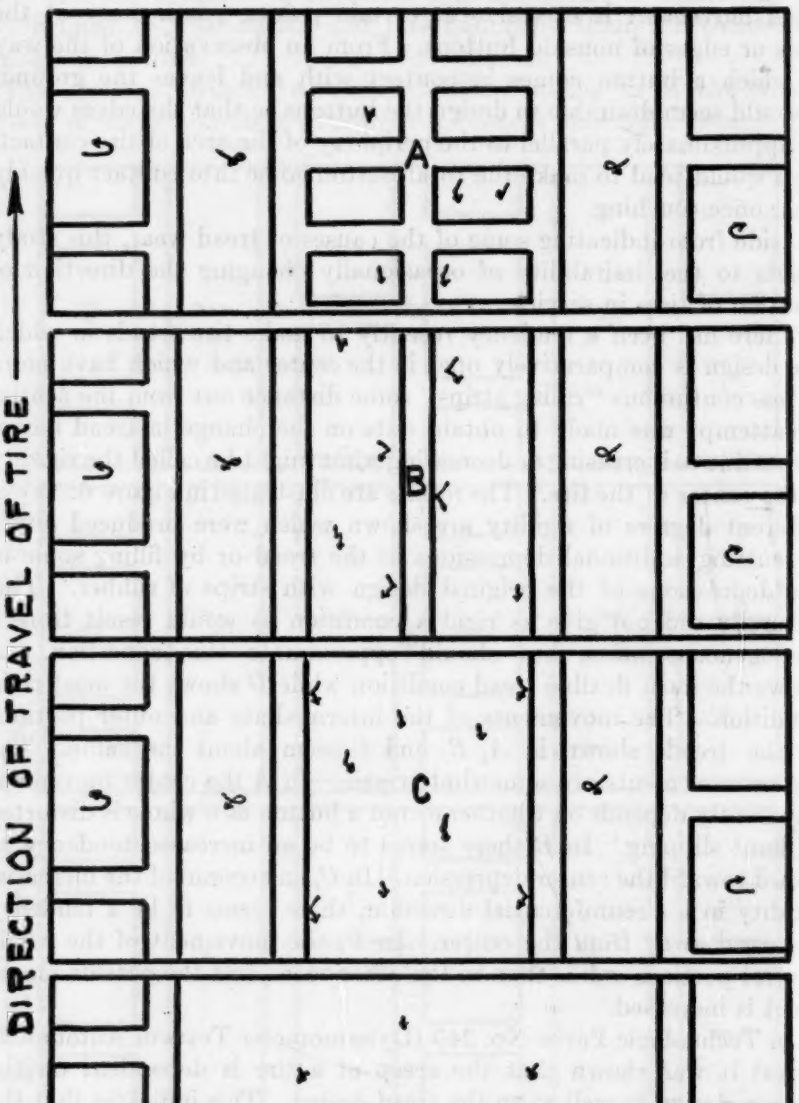

FIG. 6.—*Drawings taken from wax records showing the effect of changing the rigidity of the center portion of a tire tread on the tread movements*

over a surface as smooth as a piece of glass or a waxed plate and that the tread movement on a rough surface may be different from that which takes place on a smooth surface. Nevertheless there will be the same tendency to slip on a rough surface as on a smooth one, and the tread movement on different surfaces will simply vary in degree, depending upon the coefficients of friction.

The inference should not be drawn from the preceding discussion that the wear of a tread is attributed entirely to the movements recorded. In actual service, of course, tread wear is dependent on other factors. For instance, high tractive efforts which cause the tire as a whole to slip, slipping due to braking, the bouncing of tires in which they actually leave the ground, and side skidding. All these affect tire wear in addition to the suggested scuffing action. In some cases it is probable that these items are the predominating factors in tire wear, but from a general observation of tires in service it is thought that in most cases scuffing is the important, or at least an important factor in producing wear. A few examples will perhaps aid in substantiating this belief: (1) The tendency of treads to "cup" is more prevalent in front than in rear tires, which is in accordance with the conclusions that tractive effort tends to reduce the movements of the outer tread and to increase center movement; (2) wearing of the edges of the buttons is obviously a scuffing action; and (3) a microscopic examination of the surface of used tires does not ordinarily show abrasion in any particular direction except, perhaps, on some of the edges of buttons. This is in accordance with the scuffing theory. Wear due to slip of the tire as a whole would show movement mainly in a circumferential direction.

If scuffing is an important cause of tire wear, a study of tread movements should have a direct bearing on the subject. The portion of the tread in contact with the ground is contracted from the normal shape and it is noted that some of this contraction takes place just before the tread touches the ground. The remainder takes place after the tread is in contact, and results in slipping. If more of the contraction can be made to take place when the tread is out of contact, it would obviously reduce slipping and thus reduce wear. This contraction is influenced by tread design, tread shape, and carcass design, and it would seem that a study of this contraction offers a promising method of attacking the problem of tread wear.

A reference to the shape of the nonskid buttons has already been made.

It was noted in several tires that there is a tendency for the tread to slip nonsymmetrically even though the tread design is symmetrical. At first this was attributed to the tire or rim being out of alignment. A closer examination and adjustment of the apparatus, however,

indicates that this is the result of some nonuniformity in the tire itself.

VI. CONCLUSIONS

Two methods have been described which have been successfully tried for observing the movement of the treads of pneumatic tires under running conditions. By the second method quite complete and reliable data can be obtained with very simple equipment. This study indicates that tread movement is probably a fundamental cause of tire-tread wear and points out how certain conditions of operation affect this movement. If desired, tread movements can be observed by one of the methods with a tire running at a considerable speed and under a tractive effort. Tread movements at low speeds and no tractive efforts, however, seem to yield most of the information desired. These results show that a study of the tread movements may yield valuable information concerning the uniformity of construction of a tire. In developing laboratory abrasion tests to simulate road wear this work shows that it is desirable to use a nonlinear abrasive movement, since most of the tread surface is abraded by a more or less curved motion.

WASHINGTON, March 24, 1928.

ABSOLUTE METHODS IN REFLECTOMETRY

By H. J. McNicholas

ABSTRACT

The theory and use of the integrating sphere in three methods of reflectometry, as proposed by Sharp and Little, Karrer, and Taylor, respectively, are discussed in connection with a new absolute method in reflectometry involving no direct use of an integrating device.

The new method is based upon a general law of reciprocity, first stated by Helmholtz, by means of which certain reciprocal relations between the reflective properties for unidirectional and diffused illumination are derived and applied in the method. Under completely diffused illumination the brightness of a sample, in general, increases with increasing angle of observation from the normal to its surface. The illumination on the sample being known, these brightness data are shown to yield (with the aid of the reciprocity law) the reflectance of the sample (ratio of total reflected to total incident light) for any manner of illumination ranging from unidirectional to completely diffused.

Equipment is described for the measurement of reflective properties of materials under either completely diffused or unidirectional illumination for various directions of observation. The samples used include various kinds of materials chosen to cover a wide range of reflectance and to represent various degrees of departure from the perfect diffusor. Comparative measurements by all the methods studied are made on these samples.

CONTENTS

		Page
I.	Introduction	30
II.	Definitions and nomenclature	31
III.	Reciprocal relations	35
IV.	New method in reflectometry	37
V.	Theory of the sphere reflectometer	41
	1. Methods of Sharp and Little and of Karrer	41
	2. The Taylor reflectometer	42
VI.	Measurement of apparent reflectance	44
	1. Description of samples	44
	2. Apparatus and method for diffused illumination	45
	3. Brightness distribution over hemispherical source	49
	4. Method for unidirectional illumination	51
	5. Calculation of reflectance	52
VII.	Discussion of data	54
VIII.	Use of sphere reflectometer	61
	1. Description of diffused-illumination reflectometer and measurements	61
	2. Evaluation of illumination on sample	65
	3. Errors in measurement of reflected light	69
	4. Design of sphere	70
	5. Measurements with the Taylor reflectometer	72

I. INTRODUCTION

In various phases of photometry and colorimetry it is often desirable to obtain an absolute evaluation of some of the reflective or transmissive properties of various diffusing media. The illuminating engineer may require a knowledge of the fraction of incident light reflected by materials forming the walls and ceiling of a room as an aid in the proper design of lighting installations. The physical stimulus of color is very often the light diffusely reflected (or transmitted) by some material, such as paper, painted surfaces, dyed fabrics, etc. In colorimetric practice it has usually been most convenient to express the reflective (or transmissive) properties of these materials in terms of some material which could be regarded as a standard, but suitable and accurate methods [1] of proven reliability are needed for the evaluation of the standard (if not the sample itself) in absolute measure—particularly in regard to variations with wave length.

The reflective and transmissive properties of a diffusing medium depend on the nature and structure of the medium, the topography of its bounding surfaces, the angular distribution of the incident luminous flux, and its spectral composition. The absolute evaluation of the reflection or transmission coefficients involves an integration of the incident and of the reflected or transmitted light with respect to all directions from the surface. The photometric integrating sphere (Ulbricht sphere), long used in the photometry of light sources, has been applied in various ways for this purpose. The theory of its use is based, however, upon the simplifying assumption that the material forming the interior surface of the sphere wall reflects incident light in accordance with the cosine law [2] of emission. It is well known that the reflection of light by all diffusely reflecting materials departs considerably from this law, and that the degree of departure depends to a large extent on the angular and spectral distribution of the incident light. The extent to which the diffuse reflective properties of the sphere wall and sample affect the performance of the sphere is a matter over which there is at present considerable uncertainty.

In this investigation some of the reflective properties of a selected group of samples are exhibited and the data applied to a study of methods used in reflectometry. A thorough analysis of the methods proposed by Sharp and Little [3] and by Karrer [4] is made. The relation of the Taylor [5] method to these is shown, along with comparative

[1] In the special case of the unidirectional transmission of light by optically homogeneous (nondiffusing) media, accurate and reliable absolute methods are available. See Report of the Optical Society of America Progress Committee on Spectrophotometry, J. Opt. Soc. Am. and Rev. Sci. Inst., **10**, p. 169; 1925.

[2] For a medium obeying the cosine law of emission, the flux in a given direction, from an element of area of the surface, is proportional to the cosine of the angle between the given direction and the normal to the emitting element.

[3] Trans. Ill. Eng. Soc. **15**, p. 802; 1920.

[4] B. S. Sci. Paper No. 415; August, 1921. Also J. Opt. Soc. Am. and Rev. Sci. Inst. **5**, pp. 96–120; 1921.

[5] Trans. Ill. Eng. Soc., **15**, p. 811; 1920. B. S. Sci. Paper No. 405; November, 1920.

measurements by the Taylor reflectometer. A general method of reflectometry is also described, involving no direct use of an integrating device.

II. DEFINITIONS AND NOMENCLATURE

Consider the sample in the form of a flat slab illuminated by an extended source subtending, in general, a solid angle 2π at the center of the sample. Let θ and ϕ (fig. 1) be the angle with the normal and azimuth angle, respectively, of an incident pencil of light, included in the elementary solid angle $d\omega$; and let θ', ϕ', and $d\omega'$, be of corresponding import for a reflected pencil. The brightness[6] distribution over the source, as viewed from the position of the sample, is represented by the function $B(\theta, \phi)$. Similarly, the brightnesses of the

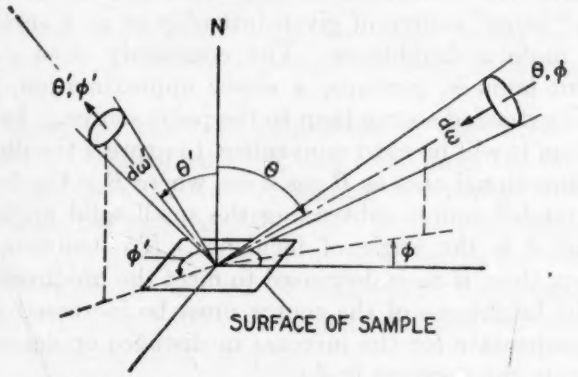

FIG. 1.—*Diagram of incident and reflected rays*

sample for a given manner of illumination and for various directions of observation (θ', ϕ') are represented by the function $B'(\theta', \phi')$.

The *reflectance*[7] of the sample is defined as the ratio of total reflected to total incident luminous flux (per unit area of surface) and designated by the symbol R. Then

$$R \equiv \frac{\text{Total reflected flux}}{\text{Total incident flux}} = \frac{\int B'(\theta', \phi') \cos \theta' d\omega'}{\int B(\theta, \phi) \cos \theta \, d\omega} \qquad (1)$$

where the integrations are taken, in both numerator and denominator, over the solid angle 2π.

As the reflectance of a given sample is a function of the spectral composition and the angular distribution of the incident flux, it is necessary to define more specifically certain groups of reflectances

[6] The brightness of the source, viewed from a given direction is proportional to the luminous flux in that direction per unit of projected area per unit solid angle. See illuminating engineering nomenclature and photometric standards; Trans. Ill. Eng. Soc., **20**, p. 629; 1925. In this work we are ultimately concerned with the ratio of brightnesses, hence no particular unit need be specified.

[7] This term has been used in the report of the Opt. Soc. Am. Progress Committee for 1922–23, on Spectrophotometry, J. Opt. Soc. Am. and Rev. Sci. Inst., **10**, p. 178; 1925.

corresponding to different types of illumination. For the samples used in this investigation the variation of reflectance with spectral composition of the source is small and will not be considered.

When the source subtends the maximum solid angle 2π at the sample and is uniformly bright over its whole extent, the illumination on the sample is *completely diffused.* When the source subtends a relatively small solid angle at the sample, the illumination is characterized as *unidirectional.* To be more specific in this case, however, we state further that the solid angular extent $d\omega$ of the incident flux shall be so small that a further decrease will not alter appreciably either the angular distribution of the reflected flux or its ratio to the incident flux. If the illumination is neither completely diffused nor unidirectional, it will be spoken of simply as *diffused.*

The source for unidirectional illumination may be represented either as a "point" source of given intensity or as a small extended source of uniform brightness. The commonly used coil-filament incandescent lamp is, perhaps, a closer approximation, physically, to the small extended source than to the point source. In the following discussion it will be most convenient to express the illumination [8] in the unidirectional case as $B \cos \theta \, d\omega$, where B is the brightness of a small extended source subtending the small solid angle $d\omega$ at the sample and θ is the angle of incidence. To maintain a definite illumination, then, if $d\omega$ is decreased to meet the unidirectional specification, the brightness of the source must be increased correspondingly to compensate for the increase in distance or decrease in area accompanying the decrease in $d\omega$.

For the convenient expression of the total illumination on the sample, in the case of a large extended source, we may imagine the actual brightness distribution $B\ (\theta, \phi)$ replaced by a uniform distribution of constant value B_0 extending over a complete hemisphere surface (subtending a solid angle 2π at the sample) and defined by the equation

$$B_0 = \frac{\int B\,(\theta, \phi) \cos \theta \, d\omega}{\int \cos \theta \, d\omega} \tag{2}$$

in which the integrals are taken over the surface of the hemisphere. This may be expressed more simply, as

$$\pi B_0 = \int B\,(\theta, \phi) \cos \theta \, d\omega \tag{3}$$

B_0 will be called the *equivalent-hemisphere brightness* of the source, and πB_0 is the total illumination on the sample. In the evaluation of the unidirectional illumination (see Section VI) it is also most con-

[8] A similar expression for the illumination from a point source would be $I\Omega$, where I is the intensity of the source and Ω is the solid angle subtended at the source by unit area of the sample.

venient for our purpose to express this illumination in terms of the equivalent-hemisphere brightness B_o. In this case equation (3) reduces simply to

$$\pi B_o = B \cos \theta \, d\omega \tag{4}$$

The equivalence of the uniform hemispherical source and the actual source for all types of illumination is only true, of course, with regard to the total illumination on the sample. They are not equivalent with regard to the angular distribution and total quantity of the reflected flux.

The total flux reflected by the sample may be represented, similarly, by $\pi B'_o$, where B'_o is the average value of the brightness function $B'(\theta', \phi')$, and defined by the equation

$$\pi B'_o = \int B'(\theta', \phi') \cos \theta' d\omega' \tag{5}$$

B'_o is obviously the brightness that the sample would have (observed in any direction) if it were a perfect diffusor [9] reflecting the same total flux.

Taking, now, the observed brightness of the sample in a given direction (θ', ϕ'), multiplied by π, as a measure of the total reflected flux, we define the *apparent* [10] *reflectance* (for the given direction of observation) as the ratio of $\pi B'(\theta', \phi')$ to the total illumination on the sample. The group of apparent reflectances for various directions of observation (θ', ϕ') will be denoted by the symbol $A(\theta', \phi')$, in which the manner of illumination is definite, but not explicitly specified. We have, then,

$$A(\theta', \phi') \equiv \frac{\pi B'(\theta', \phi')}{\pi B_o} = \frac{B'(\theta', \phi')}{B_o} \tag{6}$$

The apparent reflectance is, obviously, the reflectance which must be assigned to the sample, if, on the assumption that it is a perfect diffusor, it is to have the observed brightness. If the illumination on the sample is one lumen per square centimeter, the apparent reflectance is numerically equal to the observed brightness expressed in lamberts.

The definition of the reflectance given in equation (1) may now be rewritten, either by direct substitutions from equations (5) and (3), or by introducing the equivalent-hemisphere brightness B_o of the

[9] A perfect diffusor is a sample obeying the cosine law of emission for any angular or spectral distribution of the incident flux. This assumes that the flux per unit solid angle in a given direction of reflection is directly proportional to the projected area of the element of surface; hence the brightness of the surface is constant for all angles of view. The perfect diffusor is a very convenient ideal reference "sample" for many purposes.

[10] The use of the word *apparent* as well as the term *reflectance* was suggested by A. H. Taylor in the 1922 report (unpublished) of the Committee on Reflectometry of the Optical Society of America.

source from (2) and the apparent reflectance $A(\theta', \phi')$ of the sample from (6). Thus:

$$R=\frac{B'_o}{B_o}=\frac{\int A(\theta', \phi') \cos \theta' d\omega'}{\int \cos \theta' d\omega'} \tag{7}$$

$$=\frac{1}{\pi} \int A(\theta', \phi') \cos \theta' d\omega' \tag{8}$$

in which the integrals are to be evaluated, as before, over the surface of a hemisphere (solid angle 2π). The expanded form of π must be retained in the expression for R when the approximate evaluation of the integrals (to be explained) is effected. The reflectance for any type of illumination is most conveniently expressed and calculated as a (weighted) mean value of the apparent reflectances for that illumination.

TABLE 1.—*Nomenclature*

Symbol	Interpretation
$B(\theta, \phi)$	Brightness distribution over a finitely extended source, as viewed in various directions (θ, ϕ) from the sample.
B_o	Equivalent-hemisphere brightness of source.
$B'(\theta', \phi')$	Brightness of sample viewed in various directions (θ', ϕ') for a definite type of illumination not explicitly specified.
B_o'	Brightness the sample would have (viewed in any direction) if it were a perfect diffusor reflecting the same total flux.
R	Reflectance. (Type of illumination not specified.)
$A(\theta', \phi')$	Group of apparent reflectances for various directions of observation (θ', ϕ') and for a definite type of illumination not explicitly specified.
Subscripts, $_{D, d, U, \theta\phi}$	Specify explicitly the type of illumination; that is, diffused $_{(d)}$, completely diffused $_{(D)}$, unidirectional $_{(U)}$, and unidirectional in the specified direction $_{(\theta, \phi)}$, respectively.

SOME ILLUSTRATIONS OF THE USE OF THE NOMENCLATURE ARE AS FOLLOWS

$R_U(\theta, \phi)$	Group of unidirectional reflectances for various directions of incidence.
$A_{\theta\phi}(\theta', \phi')$	Group of apparent unidirectional reflectances for a particular direction of illumination (θ, ϕ) and various directions of observation.
$A_U(\theta, \phi; \theta', \phi')$	Complete set of apparent unidirectional reflectances for all directions of incidence and observation. The first-named angles always denote the direction of incidence; the last-named angles, the direction of observation.

Subscripts will be used to designate explicitly a specific type of illumination, as explained in Table 1. Thus, for completely diffused illumination, the reflectance is

$$R_D=\frac{\int A_D(\theta', \phi') \cos \theta' d\omega'}{\int \cos \theta' d\omega'} \tag{9}$$

The complete group of unidirectional reflectances for various directions of incidence are represented by

$$R_U(\theta, \phi) = \frac{\int A_U(\theta, \phi; \theta', \phi') \cos \theta' d\omega'}{\int \cos \theta' d\omega'} \tag{10}$$

It is of interest to note at this point that the reflectance for any manner of diffused illumination may also be expressed as a mean value of the reflectances for unidirectional illumination. The group of unidirectional reflectances $R_U(\theta, \phi)$ constitute a function given over the surface of an imaginary hemisphere with the sample at the center of its base. The diffuse reflectance R_d is then a mean value of the function $R_U(\theta, \phi)$ averaged over the hemisphere, each unidirectional reflectance being weighted by the brightness of the source $B(\theta, \phi)$ in the corresponding direction and by the factor $\cos \theta \, d\omega$. These factors together give the portion of the total illumination of the sample which is received through an element of the hemispherical surface. Hence we may write

$$R_d = \frac{\int R_U(\theta, \phi) \, B(\theta, \phi) \cos \theta d\omega}{\int B(\theta, \phi) \cos \theta \, d\omega} \tag{11}$$

and for a uniform source (completely diffused illumination)

$$R_D = \frac{\int R_U(\theta, \phi) \cos \theta \, d\omega}{\int \cos \theta \, d\omega} \tag{12}$$

III. RECIPROCAL RELATIONS

As a consequence of a general law of reciprocity, first stated by Helmholtz,[11] important reciprocal relations between certain groups of reflection coefficients may now be derived. A statement of the general law, as applied to the case here considered, is that the elementary pencils of Figure 1 are reversible with regard to both direction and angular flux density.[12] Because the angular flux density in the direction of incidence is the same in both the direct and reciprocal cases, it follows from the law of reciprocity that the angular flux density in the direction of reflection is also the same in both cases, or

$$B'_{\theta\phi}(\theta', \phi') \cos \theta' = B'_{\theta'\phi'}(\theta, \phi) \cos \theta \tag{13}$$

[11] Helmholtz: Physiological Optics, 3d ed. 1909; translated by J. P. C. Southall and published by the Optical Society of America, 1924; Vol. I, p. 231. Vorlesungen über die Theorie der Wärme Herausgegeben von F. Richarz, Leipzig, J. A. Barth; 1903, p. 161. The loss in flux density which an infinitely narrow bundle of rays of definite wave length and state of polarization undergoes on its path through any medium by reflection, refraction, absorption, and scattering is exactly equal to the loss in flux density suffered by a bundle of the same wave length and polarization pursuing an exactly opposite path. Certain restrictions to the law were stated by Helmholtz, which have, however, no bearing on the present work.

[12] Angular flux density in a specified direction from a small emitting surface of brightness B is equal to B multiplied by the projected area of the surface in the direction considered.

Multiplying both sides of the equation by $\pi/Bd\omega$, we have

$$\frac{\pi B'_{\theta\phi}(\theta', \phi')}{B \cos \theta \, d\omega} = \frac{\pi B'_{\theta'\phi'}(\theta, \phi)}{B \cos \theta' d\omega}$$

The denominators on each side of this equation express the illuminations of the sample in the direct and reciprocal cases, respectively. Using equation (4) and definition (6), it becomes

$$A_{\theta\phi}(\theta', \phi') = A_{\theta'\phi'}(\theta, \phi)$$

or, more generally expressed (Table 1)

$$A_U(\theta, \phi; \theta', \phi') = A_U(\theta', \phi'; \theta, \phi) \tag{14}$$

The apparent unidirectional reflectances for all directions of incidence and observation are thus seen to form a symmetrical function of the pairs of variables θ, ϕ and ϕ', θ'; a condition which (incidentally) must be satisfied by any theoretical or empirical formula used to represent the reflection characteristics of a sample.

By averaging the function A_U $(\theta, \phi; \theta', \phi')$ over a hemisphere (solid angle 2π), with respect to the pair of variables (θ', ϕ'), we obtain the reflectances for unidirectional illumination, as in equation (10). Averaging the same function again over the same limits with respect to the variables (θ, ϕ), obviously yields the apparent reflectances for completely diffused illumination. As the pairs of variables (θ, ϕ) and (θ', ϕ') (defining directions of incidence and observation, respectively) are interchangeable by the general reciprocal relation, equation (14), we may write

$$\frac{\int A_U(\theta,\phi; \theta',\phi') \cos \theta \, d\omega}{\int \cos \theta \, d\omega} = \frac{\int A_U(\theta,\phi; \theta',\phi') \cos \theta' d\omega'}{\int \cos \theta' d\omega'}$$

when θ' and ϕ' on the left-hand side of the equation are equal to θ and ϕ, respectively, on the right-hand side. Otherwise stated, we have, by definition

$$A_D(\theta',\phi') = R_U(\theta,\phi)$$

when $$(\theta',\phi') = (\theta,\phi) \tag{15}$$

Thus the apparent reflectance for completely diffused illumination is equal to the reflectance for unidirectional illumination, when the direction of observation in the first case is the same as the direction of incidence in the second case. In other words, they are both identical functions of the direction of observation (θ', ϕ') and the direction of incidence (θ, ϕ), respectively.

IV. NEW METHOD IN REFLECTOMETRY

To obtain the reflectance for unidirectional illumination, the necessary integration (with respect to direction) of the reflected flux, if not performed by some approximate integrating device (such as the Ulbricht sphere), must be done by actual measurements of the angular flux density of the reflected light in various directions from the sample and performing the operations indicated in equation (10). This generally requires a large number of observations and considerable computation.

Given the apparent reflectances for completely diffused illumination, however, the group of unidirectional reflectances are known at once (by equation (15)), and the reflectance for any type of illumination, ranging from unidirectional to completely diffused, may be readily computed by taking properly weighted mean values (using equations (11) or (12), which may be reduced to simpler form in the manner discussed later in Section VI).

An arrangement providing completely diffused illumination of known amount, with means for observing the brightness of the sample at any desired angle from the normal in one azimuth, is, then, an absolute reflectometer of a most general type, depending on no theory whatever of the action of an integrating device. Because of the symmetry of the illumination in this case brightness measurements for other azimuths may be made (if desired) by rotation of the sample to different positions in its own plane.

Although the preceding sections contain an adequate proof of the above statements, it will be instructive, nevertheless, to apply the general theory to a particular case in order to bring out the essential features of the method and to illustrate clearly the actual integrating process involved. For these purposes the sources for completely diffused and unidirectional illumination will be constructed in a specified manner, so that a definitely known relation exists between the illuminations on the sample as received from each of the sources.

The first step in the demonstration of the method will be an application of the integral reciprocal relation, equation (15), to derive the relation that must exist in this case between the total reflected flux for the unidirectional illumination and the reflected flux for the completely diffused illumination. Let B (fig. 2 (a)) represent the brightness of a small luminous area subtending a small solid angle $d\omega$ at the sample and satisfying the present requirements in a source for unidirectional illumination. The illumination on the sample is $B \cos \theta \, d\omega$. The reflected flux is distributed in an irregular manner, as indicated in the figure, and a measurement of its total

quantity is desired. Let $F_{\theta\phi}$ be the total reflected flux per unit solid angular extent of the incident flux. Then

$$R_U(\theta,\phi)=\frac{F_{\theta\phi}\,d\omega}{B\cos\theta\,d\omega}$$

Let us now construct the source for completely diffused illumination by extension of the source for unidirectional illumination uniformly over the surface of a hemisphere, keeping its brightness constant (fig. 2 (*b*)). Let $f_D(\theta', \phi')$ represent the angular flux density in the direction (θ', ϕ') for the hemspherical source of uniform brightness B. The total illumination is πB and the brightness of the sample, $B'(\theta', \phi')$, viewed from direction (θ', ϕ'), is $f_D(\theta', \phi')/\cos\theta'$. Then

$$A_D(\theta', \phi')=\frac{\pi B'_D(\theta', \phi')}{\pi B}=\frac{f_D(\theta', \phi')}{B\cos\theta'}$$

and, by equation (15) with the above expression for $R_U(\theta, \phi)$

$$F_{\theta\phi}=f_D(\theta', \phi') \tag{16}$$

when

$$(\theta, \phi)=(\theta', \phi')$$

This equation is merely a restatement of the integral reciprocal relation, equation (15), and is valid only for the special arrangement of sources here considered.

We will now make use of the general reciprocity law, as first stated in the preceding section, to reestablish equation (16) in a manner chosen specifically to demonstrate the integration process involved. For this purpose a particular type of sample is employed, having no regularity in its body or surface structure which would cause the apparent reflectances for a given type of illumination to depend on the orientation of the sample in its own plane.

Let light be incident in the solid angle $d\omega$ (as in fig. 2 (*a*)) and a photometer arranged to observe the sample in a direction (θ', ϕ') for which $\theta'=\theta$ and $\phi'=\phi+\pi$ (direction of regular specular reflection). Let this photometer be constructed to measure all the light reflected in a solid angle $d\omega'$—equal in all respects to $d\omega$. Imagine the sample now transformed into a perfect mirror *without changing its reflectance*. The photometer than measures the total quantity of light which was diffusely reflected from the sample in its original state. Keeping the position of the photometer and the reflectance of the transformed sample constant, let the mirror surface be slightly roughened and some body reflection added, if desired, so that the reflected flux is no longer wholly contained in the solid angle $d\omega'$ but is spread out into a larger solid angle $\omega.'$ The photometer no longer measures the total reflected flux, but now reads a lower value. Let the line M (fig. 2 (*a*)), in the plane of the paper, represent the direc-

tion of specular reflection and let N be some other direction of reflection not necessarily contained in the same plane. Arrange an additional source, equal in all respects to the first source, with line N as the direction of incidence. In accordance with the general reciprocity law, the flux density of the reflected light in the direction N due to the first source is the same as that in the direction (θ, ϕ) due to the second source. The reflective properties of the sample chosen are such that we may now rotate the second source, with the incident and reflected beams, about the normal to the sample as an axis, without altering the flux densities or the angular relation between the beams, until the direction of the reflected beam under consideration coincides with the direction M of the photometer.

Considering in the same manner all directions of reflection of the incident beam from the first source, the result is a gradual extension of the original source (keeping its brightness constant), each incre-

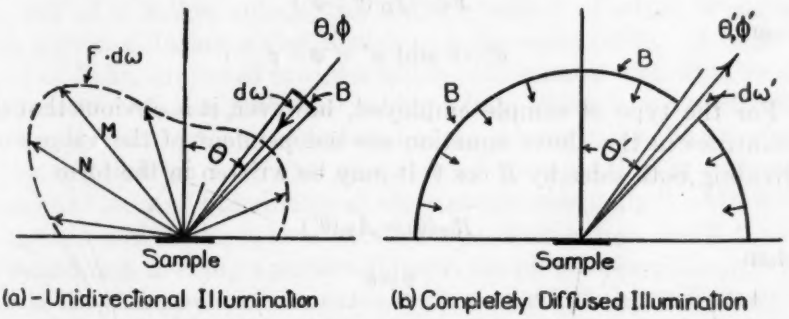

FIG. 2.—*Illustration of the application of the integral reciprocity law to reflectometry*

ment of area increasing the photometer reading slightly, until the original reading for the perfect mirror sample is completely restored. When this condition is attained, the solid angular extent of the source (as subtended at the sample) corresponds in magnitude and shape to the solid angular extent ω' of the reflected flux; in other words, for each direction of reflection (θ', ϕ') there is now a corresponding direction of incidence (θ, ϕ) such that $\theta = \theta'$ and $\phi = \phi' - \pi$. For every pencil of rays scattered out of the original solid angle $d\omega'$ by the altered mirror sample there is now an equal pencil of rays scattered into the photometer from a different part of the extended source.

The substituted mirror sample may be continuously modified, introducing body reflection as desired, until its reflective properties are exactly the same as the original sample, the reflectance of which is required. The source is simultaneously extended until it subtends if necessary a complete hemisphere at the sample. During these changes the reading of the photometer remains constant and measures the total reflected flux for the original unidirectional illumination.

The integration process involved in this experiment is evident. Instead of adding direct measurements of the angular flux density in the large number of directions from the sample (using equation (10)) or inventing a device to gather up automatically a known portion of the irregularly reflected flux and project it in one direction into a photometer, we may keep the photometer position fixed and effectively move the source about—covering all angles of incidence and adding the (unweighted) readings of the photometer for the different positions of the source. As the integrating sphere is used to obtain a direct measurement of the total reflected flux, so here the uniform hemispherical source and the reciprocity law are combined to obtain the same result by a single measurement in one direction from the sample.

The result may be expressed in the terms used above. We have, then,

$$F_{\theta\phi}=f_D(\theta', \phi')$$

when

$$\theta'=\theta \text{ and } \phi'=\phi+\pi$$

For the type of sample employed, however, it is obvious that the quantities in the above equation are independent of the value of ϕ. Dividing both sides by $B \cos \theta$, it may be written in the form

$$R_U(\theta)=A_D(\theta')$$

when

$$\theta=\theta'$$

In the more general case (equations (15) and (16)), where no restrictions are made on the type of sample considered, it is necessary that the direction of observation for completely diffused illumination (uniform hemispherical source) be in the same azimuth as the direction of incidence for the unidirectional illumination.

The theories of the instruments which have been devised for the direct integration of the reflected flux are based upon assumptions which are not always satisfactorily realized in practice (see Sections V and VIII). Moreover, it is usually difficult to obtain a sufficient illumination on the sample from one direction to enable the use of a spectrophotometer for the measurement of absolute *spectral* reflectances.

The method here described has its theoretical basis in the reciprocity law, the truth of which can not be doubted. Its general applicability to the measurement of all the reflection coefficients commends its use. It has the further advantage that the source, being extended over a hemisphere, may be readily constructed to bring a large number of lamps into use, thus obtaining a sufficient illumination on the sample for precise spectrophotometric measurements throughout the whole visible spectral range.

An equipment of this kind and its method of use (without the spectrophotometer) is described in detail in Section VI. The experimental errors likely to result from an incomplete diffusion of the illumination, in the evaluation of the constant of the instrument $1/B_0$, and in the measurement of sample brightness are there fully discussed.

Inasmuch as the quantities previously defined and the reciprocal relations derived may all be stated in an analogous manner for the transmitted flux, the method here described is equally applicable to the measurement of the analogous transmission coefficients.

V. THEORY OF THE SPHERE REFLECTOMETER

1. METHODS OF SHARP AND LITTLE AND OF KARRER

In these methods the sample forms a relatively small portion of the wall of a hollow sphere, the interior surface of which is coated with a good diffusing material such as magnesium oxide. A narrow beam of light, projected into the sphere, illuminates directly a small spot on the wall, the first reflected light from which is screened from the sample. Assuming the material of the sphere wall to be a perfect diffusor, it follows from the geometry of the sphere that any one element of the wall illuminates all other elements equally.[13] Multiple reflections within the sphere increase this illumination many times. If, in addition to being a perfect diffusor, the reflectance of the sphere wall is the same over all its parts, each element of the wall receives the same quantity of light from every other element (excluding the directly illuminated spot). The area of the sphere wall occupied by the sample is assumed to be so small that its presence or absence does not appreciably affect the illumination of the remaining part. Under these conditions the brightness B of the sphere is constant over all its parts. It serves as an extended source of uniform brightness subtending a solid angle of 2π at the sample. The illumination on the sample is completely diffused and of total amount πB (by equation (3)).

In the use of the sphere the sample is observed in a fixed direction from the normal to the surface and its brightness B' compared with that of the adjacent sphere wall; that is, with that of the source. Assuming the aforesaid conditions to be exactly realized in the construction of the sphere, the quantity measured is the apparent reflectance for completely diffused illumination and a particular direction of observation. This quantity is always equal to the reflectance R_D (for the same illumination) for at least one direction of observation (by equation (7)), but not for all directions of observation unless the reflective properties of the sample are such that the brightness

[13] Sumpner, Phil. Mag., **35**, p. 81; 1893. Ulbricht, Electrotechn. Zs., **21**, p. 595; 1900; **26**, p. 152; 1905.

(under completely diffused illumination) is *independent of the angle of view*. When this condition is satisfied, the total reflected flux is $\pi B'$ (equation (5)), and we have

$$R_D = \frac{B'}{B}$$

Because this sphere method theoretically gives the reflectance for the extreme case of the perfect diffusor (for which the brightness is, by definition, independent of the angle of view), and for purely specular reflection, as in the case of a metal mirror (for which the unidirectional reflectance is nearly independent of the angle of incidence), it has been assumed that the correct value of the reflectance R_D would be obtained for the case of any gradation of mixed specular and diffuse reflection between these extremes.[14]

The incorrectness of this assumption was first pointed out by Walsh,[15] who used an empirical expression to represent the reflection characteristics of a sample and showed by his calculations the possibility of large differences between the apparent reflectance, as measured with the sphere, and the true reflectance. Further results of the computations by Walsh are not substantiated, however, in the present investigation. (See Section VII.)

It is obvious that the sphere, as here used, has no integrating action whatever on the reflected flux. It serves merely as a means of obtaining a completely diffused illumination on the sample. The angular flux density is measured in one direction of reflection only (usually nearly normal to sample), and it is only when this direction is properly chosen for each sample (see Section VIII) that the reflectance R_D is obtained.

In the light of the reciprocity law this use of the Ulbricht sphere may better be regarded as a special case of the general method of reflectometry discussed in the preceding section. Then the quantity measured should be the reflectance for unidirectional illumination at a specified angle of incidence, and the diffusing properties of the sample itself need not be considered in the method.

2. THE TAYLOR REFLECTOMETER

In this instrument the sample likewise forms a small portion of the wall of a hollow sphere, the interior surface of which is covered with a good diffusing material of high reflectance. A narrow beam of light is projected into the sphere, either on the sample at a specified angle from the normal or on another portion of the sphere wall, as desired. A photometer compares the brightness of a third portion of the wall (shaded from the sample by an opaque screen) under two conditions: (1) When the projected beam is incident on the sample,

[14] See footnotes 3 and 4, p. 30.

[15] Trans. Ill. Eng. Soc., **18**, p. 475; 1923.

and (2) when it is incident on the sphere wall. The brightness of the observed spot is due in the first case to light reflected once from the sample and then multiply reflected from the sphere wall. The brightness in the second case is due to the light multiply reflected from the sphere wall only. The ratio of these two brightnesses gives, under certain restrictions, the reflectance of the sample.

The area occupied by the sample must be sufficiently small to be ineffective in altering the observed ratio of brightnesses. The sphere wall must also be a perfect diffusor with uniform reflectance over all its parts. Under these conditions the irregularly reflected flux from the sample is accurately integrated with respect to all directions of reflection, and a definitely known portion of the total reflected flux is projected into the photometer.

Consider the flux reflected from the sample in the direction (θ', ϕ') and falling on a small area a of the sphere wall. This area subtends a solid angle $d\omega$ at the sample, and if $f(\theta', \phi')$ be the angular flux density in the direction (θ', ϕ'), the flux incident on the element a is $f(\theta', \phi')\, d\omega$. The reflected flux is $R'f(\theta', \phi')\, d\omega$, where R' is the reflectance of the sphere wall.

The element a illuminates all other elements of the sphere wall equally; hence the illumination of the observed spot is

$$\frac{R'f(\theta', \phi')\, d\omega}{A}$$

where A is the total area of the sphere wall. Multiple reflections in the sphere now increase this illumination by the factor [16] $\frac{1}{1-R'}$. Hence, the total illumination of the observed spot, due to the portion of the total reflected flux under consideration, is

$$\frac{R'}{A(1-R')} f(\theta', \phi') d\omega$$

It is independent of the position of the element a but is proportional to the illumination of the element received from the sample.

The observed spot always sends a definite fraction of the total incident flux into the photometer, regardless of the angular distribution of the incident flux. Its brightness dB_s is R'/π times its total

[16] See Karrer, B. S. Sci. Paper No. 415, August, 1921, p. 215; also Taylor and Rosa, B. S. Sci. Paper No. 447; August, 1922, p. 307.

If F be the total flux projected (or emitted) into an inclosure with perfectly diffusing wall (such as the hollow sphere), the average total illumination E of the wall is

$$E = \frac{F}{A(1-R')}$$

where A is the total area of the wall and R' its average reflectance. The average direct illumination E_d is F/A, hence

$$E = \frac{E_d}{1-R'}$$

illumination. Hence,

$$dB_s = \frac{R'^2}{\pi A(1-R')} f(\theta', \phi')d\omega$$

Considering, now, in the same manner the flux reflected in all directions from the sample, the total brightness of the observed spot is

$$B_s = \frac{R'^2}{\pi A(1-R')} \int f(\theta', \phi')d\omega = kF'$$

where the integral is taken over the solid angle 2π, F' is the total reflected flux, and k is the constant factor outside the integral sign.

Let F be the total flux projected into the sphere on to the sample. To evaluate F it is projected on to the sphere wall and, by exactly the same procedure as before, we find the brightness B_w of the observed spot to be in this case

$$B_w = kF$$

Hence, the reflectance R of the sample is

$$R = \frac{F'}{F} = \frac{B_s}{B_w}$$

In this method it is obvious that no assumption is made in regard to the diffusing properties of the sample. The instrument theoretically measures the reflectance for unidirectional illumination at a specified angle of incidence.

VI. MEASUREMENT OF APPARENT REFLECTANCE

1. DESCRIPTION OF SAMPLES

The samples used include various kinds of material selected with respect to two widely variable characteristics, namely, the degree of departure from the perfect diffusor (extreme case represented by a mirror) and the reflectance. These characteristics are, in general, functions of the spectral composition of the incident light and its angular distribution. The purposes of this investigation have been served, however, by limiting the choice of samples to those approximately neutral in color; so that the spectral composition of the incident and reflected light need not be taken into consideration, and the complications of heterochromatic photometry, or of spectrophotometry, are thereby avoided. Likewise, samples having a regular body structure or surface texture (such as a distinct weave or corrugation) are not included, as they complicate the measurements by introducing another variable (an azimuth angle) and are not of particular interest here.

The samples are listed in Table 2, with the reflectances and other data. The paper and cloth samples were mounted on aluminum

plates (using dry-mounting tissue) to insure flatness of surface and permanence of form. Further description of the samples, indicative of their departure from the perfect diffusor, is afforded by the curves (to be described) in Figures 5, 6, and 7.

2. APPARATUS AND METHOD FOR DIFFUSED ILLUMINATION

In this section equipment is described with which the apparent reflectances for diffused illumination may be measured and the reflectance computed (by equation (9)). The essential parts of the apparatus are shown in Figure 3. The sample S is supported from below against the rectangular opening O in the center of and parallel to the base of a milk-glass hemisphere M, the outer surface of which is illuminated by 104 small tungsten filament lamps mounted on the hemispherical shell Al, which is concentric with the milk-glass hemisphere. The interior surface of the aluminum hemisphere and the whole base is covered with a deposit of magnesium oxide. The lamps are arranged on six parallels of latitude, equally spaced from the first ring of four lamps (about the pole) to the base. The spacing of the lamps on each ring is decreased progressively toward the bottom to partly compensate for the decreased direct illumination of the lower part of the milk-glass hemisphere. The current in each ring of lamps is separately adjustable.

To locate points on the hemisphere and specify directions from the normal to the sample (polar axis of hemisphere), let θ (as in fig. 1) be the angle from the polar axis and ϕ the azimuth angle measured (clockwise from above) from the meridian plane through N. The sample is under diffused illumination from the hemispherical source and may be viewed at angles of 0, 12.0, 25.5, 39.0, 52.5, 66.0, and 78.5°, respectively, through seven small holes cut through the milk-glass hemisphere along the 180° meridian and corresponding holes in the outer hemisphere. The tube T, with small aperture at a, extends from each hole in the outer hemisphere to within a few centimeters of the milk glass and serves to prevent the entrance into the optical observing system of the direct light from the hemisphere. These tubes are blackened on the inside and coated on the outside with magnesium oxide. The arm A, supporting prisms P_3, P_2, P_1, and lenses L_2, L_1, may be rotated about a horizontal axis through the center of the hollow bearing B and held fixed in any position by a clamp C.

Brightness measurements at any of the above angles of view are made as follows: With the sample in place at S and the arm clamped in position at the desired angle, a beam of light from the sample is directed by the prisms and lenses along the axis of rotation of the arm and serves to illuminate one-half of the biprism photometric field B–L. This field is viewed through the aperture E. The other

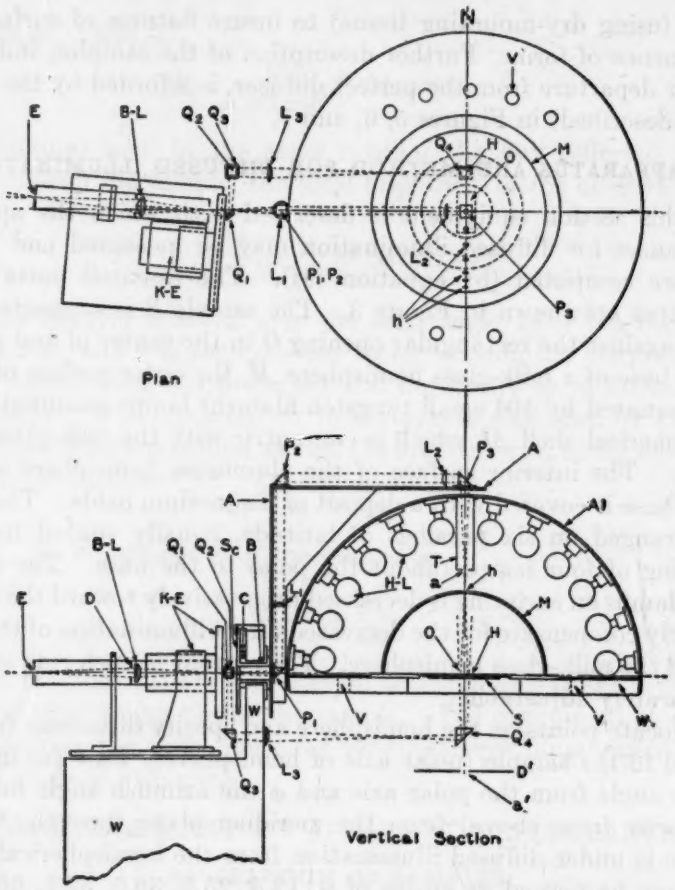

FIG. 3.—*Apparatus for the measurement of apparent reflectances under completely diffused illumination*

Lower diagram is vertical section through polar axis of hemisphere. Upper diagram is view with outer hemisphere and other supports removed.

M, milk-glass hemisphere, 9 inches in diameter, held in position on aluminum base plate. *Al*, aluminum hemisphere, 2 feet in diameter (built up in sectors), supporting lamps and serving as a reflector. *H-L*, hemisphere lamps; 9 volt, 27 c. p. automobile headlight lamps, 104 in all; filaments approximately 13 cm from milk-glass hemisphere. *S*, sample held in position by clamp (not shown). *O*, opening in base plate for sample, size 6 by 2 cm. Surface of sample is 1 mm below inner surface of hemisphere base plate. *h*, holes in milk-glass hemisphere (each 6 mm diameter) through which sample is viewed at different angles. P_1, L_1, P_2, P_3, L_2, prisms and lenses of "sample" beam. Q_1, Q_2, Q_3, L_3, prisms and lenses of comparison beam. *A*, rotating arm supporting prisms and lenses of sample beam. *B*, hollow bearing for rotating arm. *C*, clamp to hold arm *A* in desired position. *Sc*, circular scale giving position of arm. *K-E*, Keuffel and Esser variable sectored disk photometer. *B-L*, biprism and lens forming photometric field. *H*, hole in base for comparison beam. *T*, tube with small aperture *a* (one tube for each angle of view) to prevent entrance of direct light from hemisphere into optical observing system. *D'*, movable opaque screen with small aperture, *a'*, serving same purpose as tube *T* in measurements of hemisphere brightness. *W*, wood supports. *V*, ventilating holes. A forced ventilation was necessary. This is not shown in diagram.

half of the field is illuminated by a beam of light proceeding from a spot on the interior surface of the milk-glass hemisphere (at $\phi=0$, $\theta=35°$) through a hole H in the base and thence by way of fixed prisms and lenses Q_4, L_3, Q_3, Q_2, Q_1 to the biprism and lens combination B–L. The brightness of this half of the field can be controlled by means of a Keuffel and Esser variable sectored disk photometer.[17]

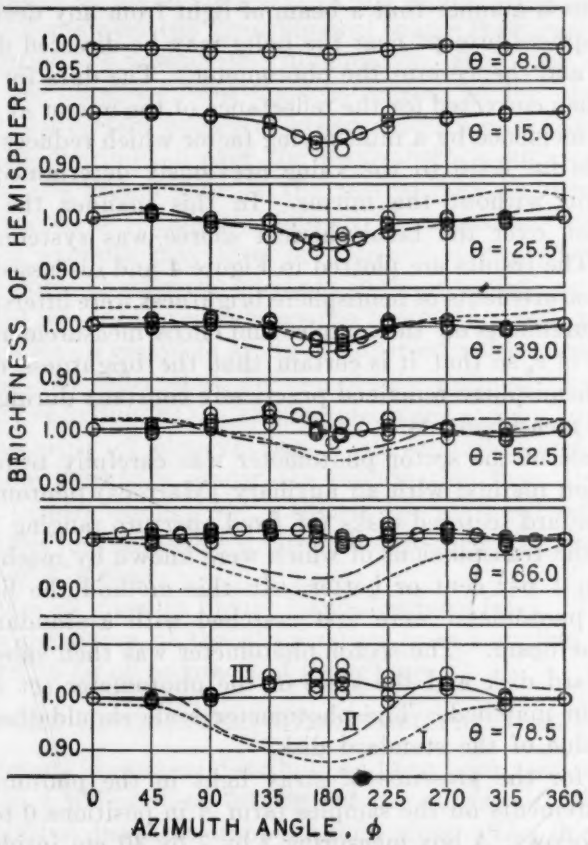

FIG. 4.—*Brightness distribution over hemispherical source*

Dotted lines = distribution I. Dash lines = distribution II. Full lines = distribution III.

By rotating the arm A from 90 to 180 °, the brightness distribution along the zero meridian of the hemisphere ($\phi=0$; $\theta=0$ to 90°) may (with the sample removed) be measured directly. With the observing arm at 145° the two beams of light proceed from the same spot on the wall; hence the brightness of this spot is taken as the unit in which all other brightness measurements, on the samples and source, are expressed. Photometric readings with the arm in this position varied, however, from time to time, due mainly to the accumulation

[17] C. W. Keuffel, J. Opt. Soc. Am. and Rev. Sci. Inst., **11**, p. 403; October, 1925.

of dust on the exposed surfaces of the prisms and lenses. Consequently, these reference readings were always taken immediately before and after each set of readings on a sample (or the source).

To measure the brightness distribution over the remainder of the hemisphere, the arm A is clamped in position at 180° and a plane silvered-glass mirror mounted at the center of the base of the hemisphere in such manner that a beam of light from any desired part of the hemisphere (except near the pole) may be directed down to the prism P_3 and thence into the photometer. The data for any value of θ are then corrected for the reflectance of the mirror at the various angles of incidence by a multiplying factor which reduces the brightness value for $\phi=0$ to the value previously determined by direct observation without the mirror. In this manner the brightness distribution over the hemispherical source was systematically explored. The results are plotted in Figure 4 and discussed later.

The measurements of hemisphere brightness were interspersed with the measurements on the samples and check measurements made at all values of θ, so that it is certain that the brightness distribution over the hemisphere remained practically constant during the course of all the measurements.

The scale of the sector photometer was carefully tested, using a substitution method with an auxiliary (Martens) photometer and a set of standard sectored disks (of fixed aperture ranging from 0.015 to 0.80), the transmissions of which were known by mechanical calibration to 1 per cent or better. In this method the fields of the auxiliary photometer were first matched with a standard sectored disk in one beam. The sector photometer was then substituted for the standard disk and the scale of the photometer set so that the fields again matched. The photometer scale should then read the known value of the standard disk.

A test for the presence of stray light in the photometric field, for measurements on the samples (arm A in positions 0 to 90°), was made as follows: A box measuring 3 by 7 by 30 cm inside was lined on the two 7 by 30 cm sides and bottom with black velvet and the other two sides covered with strips of silvered-glass mirror. This box was mounted below the base of the hemisphere with its long axis coincident with the polar axis of the hemisphere and the mirror sides perpendicular to the zero meridian plane. An aperture in the top of the box coincided with the sample aperture at O (fig. 3). The action of the mirrors permitted light to be taken only from the black bottom surface of the box for each position of the arm A, and the box thus served as a "sample" of practically zero reflectance. The photometer readings with this box in place were practically zero for each position of A, hence the stray light present was entirely negligible. For measurements of hemisphere brightness (arm A in posi-

tions 90 to 180°) a diaphragm D' was inserted in the focal plane of the lens L_2 with small aperture a' just large enough to allow the beam to pass through. This corresponds to the aperture a and prevents the entrance into the optical system of extraneous light from the hemisphere.

The evaluation of the illumination on the sample from the brightness measurements over the hemispherical source is discussed in the following section. Knowing the illumination, then, the apparent reflectances are obtained from the brightnesses of the sample (by equation (6)) for certain angles of observation in one azimuth. If the brightness distribution over the hemisphere is sufficiently uniform so that the illumination of the sample may be regarded for practical purposes as completely diffused, the apparent reflectances for any other azimuth may then be obtained if desired, by rotation of the sample to different positions in its own plane and repeating the brightness measurements on the sample for each new position. In this way a complete group of apparent reflectances may be obtained and the reflectance for completely diffused illumination computed (by equation (9)). The samples were chosen, however, to avoid the necessity of observations in all azimuths; and they all gave the same brightness under the illumination from the hemisphere when turned through 90°. Hence, the apparent reflectances of these samples for completely diffused illumination may be regarded as functions of θ' alone.

The data are all given in Figure 5 and discussed later. The effect of the small departure of the illumination from complete diffusion will be shown to be of no practical importance.

3. BRIGHTNESS DISTRIBUTION OVER HEMISPHERICAL SOURCE

Three different brightness distributions have been used, each corresponding to a different adjustment of the currents in the lamps and their relative distances from the milk glass. The thickness of the milk-glass hemisphere varied from 1½ to 3 mm (approximately) over its different parts, causing corresponding variations in the brightness of the inner surface due to its variable transmission. The decreased transmission of the direct light from the lamps by the thicker portions of the hemisphere is partly compensated, however, by a greater reflection by these thicker parts of the light incident on the inner surface. The regions of low brightness in Distributions I and II are due primarily to the greater thickness. This was compensated in Distribution III by moving the lamps closer to the milk glass and by readjustment of the currents.

The data for Distribution III are all plotted as circles in Figure 4. Each single circle at $\phi = 0$ is the mean of several points determined for this azimuth. The dip in the curves at $\phi = 180°$ ($\theta = 15.0$, 25.5,

and 39.0°) is not due to the presence of the holes in the hemisphere but to an appreciable shading of these regions of the hemisphere by the tubes T (fig. 3). The dip is not shown for higher values of θ because of its small angular extent. With the exception of these small regions, the brightness distribution over the hemisphere (for Distribution III) is constant to within ± 4 per cent of the average brightness and is constant to within ± 2 per cent over 90 per cent of the whole hemisphere. The brightness along the zero meridian is constant to within ± 1 per cent. Measurements were also made for values of θ equal to 32, 45, and 59°. These data are not shown in Figure 4 but were used in the calculation of the total illumination.

The equivalent-hemisphere brightness of the source is computed from these data by equation (2). Writing $d\omega = \sin\theta\, d\theta\, d\phi$ and evaluating the integrals over the hemisphere, we have

$$B_0 = \frac{\int_0^{2\pi}\int_0^{\pi/2} B(\theta,\phi)\cos\theta\sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi/2}\cos\theta\sin\theta\, d\theta\, d\phi}$$

$$= \frac{\pi\int_0^{\pi/2}\sin 2\theta\, d\theta \frac{1}{2\pi}\int_0^{2\pi} B(\theta,\phi)\, d\theta}{\pi\int_0^{\pi/2}\sin 2\theta\, d\theta}$$

$$= \int_0^{\pi/2} \overline{B}(\theta)\, K(\theta)\, d\theta$$

$$= \sum_0^{\pi/2} \overline{B}(\theta)\ K(\theta), \text{ approximately} \qquad (17)$$

where $\overline{B}(\theta)$ is the mean value of $B(\theta, \phi)$, averaged with respect to ϕ, and $K(\theta)$ is a set of weights summing to unity.

$$K(\theta) = \frac{\sin 2\theta}{\int_0^{\pi/2}\sin 2\theta\, d\theta} = \frac{\sin 2\theta}{\sum_0^{\pi/2}\sin 2\theta}, \text{ approximately} \qquad (18)$$

A curve was drawn showing $\overline{B}(\theta)$ as a function of θ, and values read from this curve at intervals of 5° were multiplied by $K(\theta)$, computed for the same intervals. The value of B_0 obtained from the summation was 0.999, for the brightness Distribution III.

The brightness Distributions I and II, represented by the dotted and dashed lines, respectively, in Figure 4, are the observed brightnesses in each case multiplied by the proper factors to give the same equivalent-hemisphere brightness as given by Distribution III. Thus, all three distributions (as represented in fig. 4) give the same total illumination on the sample.

4. METHOD FOR UNIDIRECTIONAL ILLUMINATION

The apparatus of Figure 3 was designed so that the hemispherical source could readily be removed. The sample was then mounted at O and a 400-watt concentrated filament lamp placed at a distance of 50 cm from O, in the vertical plane through N and O, and including the normal to the sample. A block of magnesium carbonate, placed in the position of Q_4, received light from the same lamp and served as a comparison source. This arrangement eliminates any effect on the photometer readings caused by variations in the intensity of the lamp.

The sample could be orientated to receive a beam of light (uncollimated) at any desired angle of incidence and the brightness of the sample observed at various angles of reflection in the plane of incidence. These brightnesses were all measured relative to the brightness of a porcelain plate, which was substituted for the sample and observed (by reflected light) at an angle of 50° for normal illumination. The brightness of this plate served as a temporary unit in which all brightness measurements on the sample were expressed.

Readings on the porcelain plate were always taken immediately before and after each set of readings on a sample, so that any steady shifting of the photometer readings (due mainly to the gradual accumulation of dust on the optical surfaces) had no effect on the brightness measurements.

To obtain the apparent reflectances, it is now necessary to evaluate the illumination on the sample or, otherwise stated, to determine the equivalent-hemisphere brightness of the source expressed in the same unit of brightness used in the measurements on the samples. For this purpose a *transmission standard* [18] was used. This consisted simply of a plate of milk glass of known apparent transmission [19] for normal observation on one side and unidirectional normal illumination on the opposite side. The transmission standard was substituted for the porcelain plate and its brightness by transmitted light (viewed normal to the surface) measured relative to the brightness of the porcelain plate (unit brightness). The illumination in both cases was normal to the surfaces. Calling this relative brightness B'', the equivalent-hemisphere brightness B_0 is determined from the definition:

$$\text{Apparent transmission} = \frac{B''}{B_0}$$

The apparent reflectances may now be obtained by equation (6). In the case of unidirectional normal illumination they can be meas-

[18] Loaned to the author by Bureau of Standards, division 1, section 5 (photometry). The calibration of this standard consisted in a determination of the brightness in lamberts of one side of the plate (observed normal to the surface) for a known illumination in lumens (incident normally on the opposite side).

[19] Apparant transmission is analogous to apparent reflectance and defined in like manner as the brightness (by transmitted light) of the sample multiplied by π and divided by the total illumination.

ured for all azimuths (if desired) by rotation of the sample in its own plane. For all the samples studied, however, the apparent reflectances in the plane of observation were found to be practically independent of the azimuthal orientation of the sample. Hence, the brightness and apparent reflectance for this type of illumination may be regarded (as in the case of completely diffused illumination) as functions of θ' alone. The data are shown in Figure 6 and are sufficient for the calculation of the reflectances.

To calculate the reflectance for any unidirectional illumination other than normal, the apparent reflectances for all azimuths of observation would be required. Complete data for this purpose could not be obtained with the above equipment. The apparent reflectances for 45° illumination and angles of observation in the plane of incidence are given in Figure 7.

5. CALCULATION OF REFLECTANCE

Owing to the choice of samples and the symmetry of the illumination, it has been shown that the apparent reflectances for both completely diffused illumination and unidirectional normal illumination (figs. 5 and 6, respectively) are independent of the azimuth angle ϕ' of the direction of observation and are functions of θ' alone. Hence equations (9) and (10) for the reflectances are simplified, and after evaluating $d\omega$, we have from (9)

$$R_D = \frac{\int_0^{\pi/2} A_D(\theta') \sin 2\theta' \, d\theta'}{\int_0^{\pi/2} \sin 2\theta' \, d\theta'} \tag{19}$$

$$= \sum_0^{\pi/2} A_D(\theta') \, K(\theta'), \text{ approximately} \tag{20}$$

and from (10)

$$R_U(0) = \frac{\int_0^{\pi/2} A_U(0; \theta') \sin 2\theta' \, d\theta'}{\int_0^{\pi/2} \sin 2\theta' \, d\theta'} \tag{21}$$

$$= \sum_0^{\pi/2} A_U(0; \theta') \, K(\theta'), \text{ approximately} \tag{22}$$

where $K(\theta')$ is defined by equation (18).

Values read from the curves of Figures 5 and 6 at 5° intervals of θ' were multiplied by $K(\theta')$ for the same intervals and the reflectance obtained from the summation. The computed reflectances for both types of symmetrical illumination are given in columns 2 and 13 of Table 2.

TABLE 2.—*Summary of data*

Sample	Completely diffused illumination									Unidirectional illumination				
	Hemispherical source; equipment of Figure 3					Results with sphere reflectometer (equipment of Figure 8; method essentially same as proposed by Sharp and Little and by Karrer				Equipment of Figure 3, modified for unidirectional illumination			Measurements with Taylor sphere reflectometer	
	Reflectance R_D	Apparent reflectance $A_D(\theta')$ for observation angles of—				Apparent reflectance $A_D(7)$ compare with columns 3 and 13	Errors in measurement of reflectance, resulting from assumption that apparent reflectance equals true reflectance for certain angles of observation; computed from columns 2, 3, 5, 6, for observation angles of—			45° incidence	Normal incidence		30° incidence	40° incidence
		0°	35°	55°	60°		0°	55°	60°	Apparent reflectance $A_U(45; 0)$	Apparent reflectance $A_U(0; 45)$	Reflectance $R_U(0)$ compare with column 3	Reflectance, Munsell instrument $R_U(30)$ compare with column 4	Reflectance, Bureau of Standards instrument $R_U(40)$ compare with column 4
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Matt papers: [1]							*Per cent*	*Per cent*	*Per cent*					
M–1	0.870	0.858	0.864	0.871	0.872	0.862	−1	0	0	0.869	0.872	0.860	----------	0.865
M–2	.517	.494	.501	.517	.525	.493	−4	0	+1	.486	.496	.492	0.498	.511
M–5	.201	.170	.180	.203	.213	.174	−15	+1	+6	.163	.165	.170	.184	.187
M–8	.045	.038	.040	.046	.048	.040	−16	+2	+7	.037	.037	.039	----------	.055
Glossy papers: [2]														
V–1	.753	.735	.740	.745	.752	.736	−2	−1	0	.712	.712	.736	.730	.742
V–2	.453	.440	.431	.434	.443	.437	−2	−4	−2	.412	.407	.441	.438	.435
V–3	.283	.257	.245	.262	.275	.240	−9	−7	−3	.218	.214	.255	.254	.246
V–5	.115	.065	.066	.093	.112	.061	−44	−19	−3	.019	.019	.067	.071	.077
Magnesium carbonate [3]	.981	.981	.981	.981	.981	.983	0	0	0	.995	1.000	.979	.977	.975
Porcelain	.800	.786	.793	.803	.807	.784	−2	0	+1	.791	.793	.785	.793	.798
White felt	.726	.665	.695	.724	.734	.672	−8	0	+1	.685	.692	.674	.695	.714
Black felt [4]	.024	.017	.019	.023	.026	.019	−29	−4	+8	.016	.016	.018	.026	.033
Aluminum (ground surface)	.321	.303	.308	.317	.322	.304	−6	−1	0	.294	.293	.306	----------	.297
Black glass: [5]														
Ground surface	.081	.053	.061	.081	.089	.056	−47	0	+10	.0465	.047	.054	.077	.069
Polished surface	.098	.043	.047	.075	.095	.043	−56	−23	−3	----------	----------	----------	.053	.066
Silvered-glass mirror [6]	.830	.830	.830	.830	.830	.810	0	0	0	----------	----------	----------	----------	----------

[1] Cardboard, coated with matt grey paint.
[2] Photographic print paper: Velox; exposed, developed, washed, and ferrotyped.
[3] Commercial block form: Surface scraped with smooth metal edge.
[4] Fine ground with "flour" carborundum.
[5] Jena smoke 3815; index of refraction 1.5313 (D lines).
[6] Silver film on back surface of ¼-inch plate glass.

VII. DISCUSSION OF DATA

The apparent reflectances for the diffused illumination represented by the brightness Distribution III [20] (fig. 4), are shown by the circles and curves in Figure 5. Measurements on some of the samples were also made for brightness Distributions I and II of Figure 4. These measurements were found, however, to be slightly incorrect in absolute value, due to stray light errors [21] in the brightness measurements. The data were subsequently corrected to give the same reflectance as obtained with Distribution III, for which, it is believed, no stray light errors were present. The corrected data are shown by the triangles and crosses, respectively, in Figure 5. As may be noted, there is good agreement between the relative values of the apparent reflectances for any one sample for each of the three different brightness distributions over the source, showing that the diffused illumination on the sample, resulting from each of these brightness distributions, is a sufficient approximation to the ideal completely diffused type of illumination for practical purposes. The three different angular distributions of incident luminous flux give sensibly the same distribution of the reflected flux and undoubtedly the same absolute value of the reflectance.

A comparison of columns 3 and 13 (Table 2) shows the equality of the unidirectional normal reflectance and the apparent diffuse reflectance for normal observation, in accordance with the reciprocal relation expressed in equation (15). Assuming this relation, then, the ordinates of the curves of Figure 5 give (as previously stated) the unidirectional reflectances for all angles of incidence. The reflectance for any type of multidirectional illumination must be given by taking a (properly weighted) mean value of the unidirectional reflectances; hence these data as a whole give some information as to the range of variation which may occur between the reflectances for various types of illumination with different kinds of materials. Thus, the reflectances for the black glass mirror or for the sample V–5 will vary under different types of illumination from a small fraction up to unity. In the case of magnesium carbonate the reflectance is (practically) independent of the manner of illumination. Its reflectance is so high, however, as to leave very little range for an appreciable variation. It would be of interest to know if a more

[20] In case of the mirror samples and the hemispherical source, the actual brightness distribution along the zero meridian was used to obtain the apparent reflectances.

[21] These measurements were made without the tubes T and the diaphragm D' (fig. 3). Consequently a considerable amount of stray light was present in the photometric field, necessitating a stray light correction to all the brightness measurements. This correction could not be determined with a high degree of accuracy. Assuming an error was made in the evaluation of the stray light, the reflectances determined by either Distribution I or II should bear a linear relation to the reflectances determined for Distribution III (for which all stray light effects were practically eliminated by insertion of the tubes T and diaphragm D'). This was found to be the case, and it may be presumed that, had the stray light error been exactly evaluated, the same absolute values of reflectance would have been obtained for Distributions I and II as were obtained or Distribution III.

highly absorbing medium could be constructed for which the reflectance would be practically independent of the manner of incidence. If, in addition, the reflectance was independent of the spectral composition of the incident light an ideal and much needed material would be available for reflection standards.

Vertical arrows on the curves of Figures 5 and 6 mark the mean ordinates (by equations (19) and (21)) and show the angles of observation for which the apparent reflectance is equal to the reflectance. In the case of completely diffused illumination, these angles are in the range between 50 and 55° for matt samples, increasing to 60° or above for glossy samples.

Similar data for unidirectional normal illumination has been given by Taylor,[22] who measured the brightness of 25 or 30 different samples at various angles of view, and found that the apparent reflectance for an angle of observation of 50° was equal to the reflectance to within 1 per cent for most of his samples. An angle of about 59° was found, however, for polished milk glass.

A very useful purpose would be served in reflectometry if this angle was more nearly the same for all kinds of samples, for then a single brightness measurement at the proper angle (for either type of symmetrical illumination) might yield the true reflectance to a sufficient approximation. In the case of unidirectional normal illumination and samples of fairly high reflectance (magnesium carbonate, porcelain, white felt, M–1 and M–2), it may be noted (fig. 6) that the apparent reflectance for an observation angle of 50° is within 1 per cent of the reflectance; but it is evident that a single brightness measurement at any one specified angle can not be generally relied upon as a sufficiently approximate method of reflectometry. The degree of approximation which may be obtained in the case of diffused illumination is shown in columns 8, 9, and 10 of Table 2 and considered later.

Samples V–1, V–2, V–3, and V–5 have a very smooth surface and consequently a distinct specular component of reflectance (fig. 7) superposed on the diffuse component. This specular component amounts to approximately 4.7 per cent of the incident light for nearly normal incidence. Its effect on the shifting of the mean ordinate [23] for unidirectional normal illumination is shown in Figure 6, whereas the mean ordinate for completely diffused illumination remains close to 60° for these samples. The magnitude of the

[22] Trans., Ill. Eng. Soc., **15**, p. 813; 1920. The quantity given by Taylor is the ratio of the apparent reflectance to the reflectance, and expressed in his paper (fig. 4) as the "ratio of specific brightness of test surface to the brightness of a perfect diffusor radiating the same total flux."

[23] In the calculation of the reflectance of these samples for unidirectional normal illumination, the diffuse component was obtained separately using equation (22) and ignoring the component of the apparent reflectance for $\theta' = 0$ which is due to the specularly reflected light. The specular component of the reflectance was measured separately, using a small diffusely emitting surface as a source which was just large enough to completely fill the photometer field with light. The brightness of this source was first observed directly and then as seen by specular reflection from the surface of the sample.

specular component is governed by the Fresnel reflection formulas. Hence, under unidirectional illumination, this component increases with the angle of incidence (while the diffuse component decreases), approaching the value of unity at grazing incidence, as the type of reflection becomes entirely specular. For completely diffused illumination the apparent reflectance of these samples consequently approaches unity for large angles of observation, but approaches a value less than unity for the other samples (having a rough surface).

It may be noted that the apparent reflectances of the mirror samples and the V samples do not appear in Figures 6 and 7 for angles of observation corresponding to the angle of specular reflection. A consideration of the definitions of brightness, apparent reflectance, and unidirectional illumination previously given, together with the well-known laws of reflection from a mirror surface, shows that the apparent reflectance for unidirectional illumination and purely specular reflection (as from a perfect mirror surface) has a value at one angle only and that value is indefinitely large. In the case of the V samples, as illustrated in Figure 7 for 45° illumination, the diffuse component of the apparent reflectance (roughly considered as due to light reflected from the body of the material only) for $\theta' = -45°$ has a finite value, which can not be separated in the observations, however, from the value of the specular component (regarded as due to surface reflection only). The broadness of the peaks on these curves (at $\theta' = -45°$) is due mainly to the finite and fixed solid angular extent of the incident luminous flux, but may also be due in part to the finite solid angular extent of the beam taken off the sample by the photometer. The illumination is no longer unidirectional (in strict accordance with the definition) for the case of specular reflection. If the surface of these samples was perfectly smooth and the solid angular extent of the incident flux allowed to decrease indefinitely (to satisfy the definition for unidirectional illumination), the bands (partly) shown in Figure 7 would become narrower and higher (presuming a satisfactory measuring instrument is used) and the value of the specular component of the apparent reflectance indefinitely large. Since no surface in nature is a perfect mirror, the apparent reflectance will always be finite, but may be difficult to measure in the cases considered. For angles of observation close to $\theta' = -45°$, the brightness results from a mixture of both body and surface reflection. If the specular reflection could be entirely ignored in the measurements, the curve for the diffuse component would probably take a form through this region as indicated by the dotted line in the case of the V–2 sample of Figure 7.

The slope of the curves for completely diffused illumination is opposite to that predicted by Walsh (loc. cit.) for his theoretical

samples. His simple empirical formula, however, only roughly represents the reflective properties of materials. Furthermore, it violates the general reciprocity condition previously stated in equation (14). Consequently, the results derived by integration of the formula do not satisfy the integral reciprocal relation expressed in equation (15). Thus, the formula makes the unidirectional reflectances independent of the direction of incidence while it allows the apparant diffuse reflectances to vary with the direction of observation, and the calculation of the brightness variation with angle of observation (for completely diffused illumination) shows a continuously decreasing brightness with increasing angle. This result is used by Walsh to explain the low value (0.88) obtained by Nutting [24] for the reflectance of magnesium carbonate His contention that this low value is due to a decrease in brightness of the carbonate for large angles of observation is untenable in view of the present data, for the brightness of magnesium carbonate at large angles of observation (75°) is sensibly the same as at smaller angles. The Nutting reflectometer theoretically measures the apparent reflectance for completely diffused illumination for an angle of observation of approximately 75°. The results obtained with this instrument would, in general, be higher than the true reflectance, but it should give the correct value for magnesium carbonate. The most probable explanation of the low value actually obtained for this substance lies in the effect of the departure of the illumination on the sample from the completely diffused type and, more particularly, its incorrect evaluation by a single brightness measurement of the source.

The curves in Figures 5, 6, and 7 are of further interest in methods of colorimetry, since they afford a comparison of the relative brightnesses of the samples under different methods of illumination. In columns 3, 11, and 12 of Table 2 the apparent reflectances (proportional to brightnesses) are tabulated for the following cases: (1) Completely diffused illumination, normal observation; (2) unidirectional normal illumination, 45° observation; (3) unidirectional 45° illumination, normal observation. The values for cases (2) and (3) are practically identical, [25] as they should be in accordance with the reciprocity law stated in equation (14).

[24] Nutting, Trans., Ill. Eng. Soc., **7**, p. 412; 1912. *See also* Karrer, B. S. Sci. Paper No. 415, p. 210; August. 1921. The principle of Nutting's method is that of two parallel infinite planes, one of which is the source and is assumed to obey the cosine law of emission. The other plane is the sample, the reflectance of which is to be measured. If the sample is a perfect diffusor, the relative brightnesses of the two planes gives the reflectance for completely diffused illumination.

[25] By the general reciprocity law (footnote 11), these two methods of illumination and observation should also be equivalent as regards spectral composition and polarization of the reflected light.

By the same relation the curves of Figure 6 can be interpreted as the apparent reflectance of the samples for normal observation and various directions of unidirectional illumination. Similarly, the

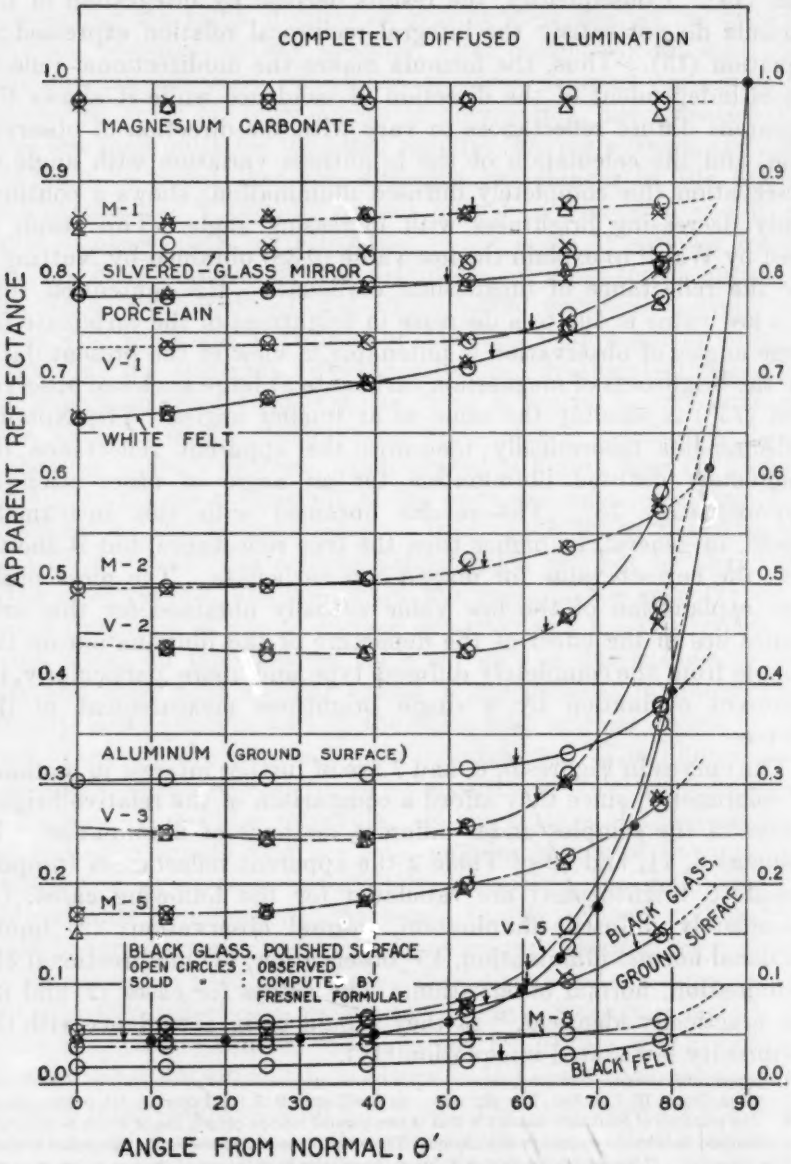

FIG. 5.—*Apparent reflectances for completely diffused illumination*

Vertical arrows on curves mark angles of observation for which the apparent reflectance is equal to the reflectance. (Reciprocal interpretation of curves: Reflectances for unidirectional illumination.)

curves of Figure 7 give the apparent reflectances for 45° observation and unidirectional illumination at various angles of incidence in the plane of observation.

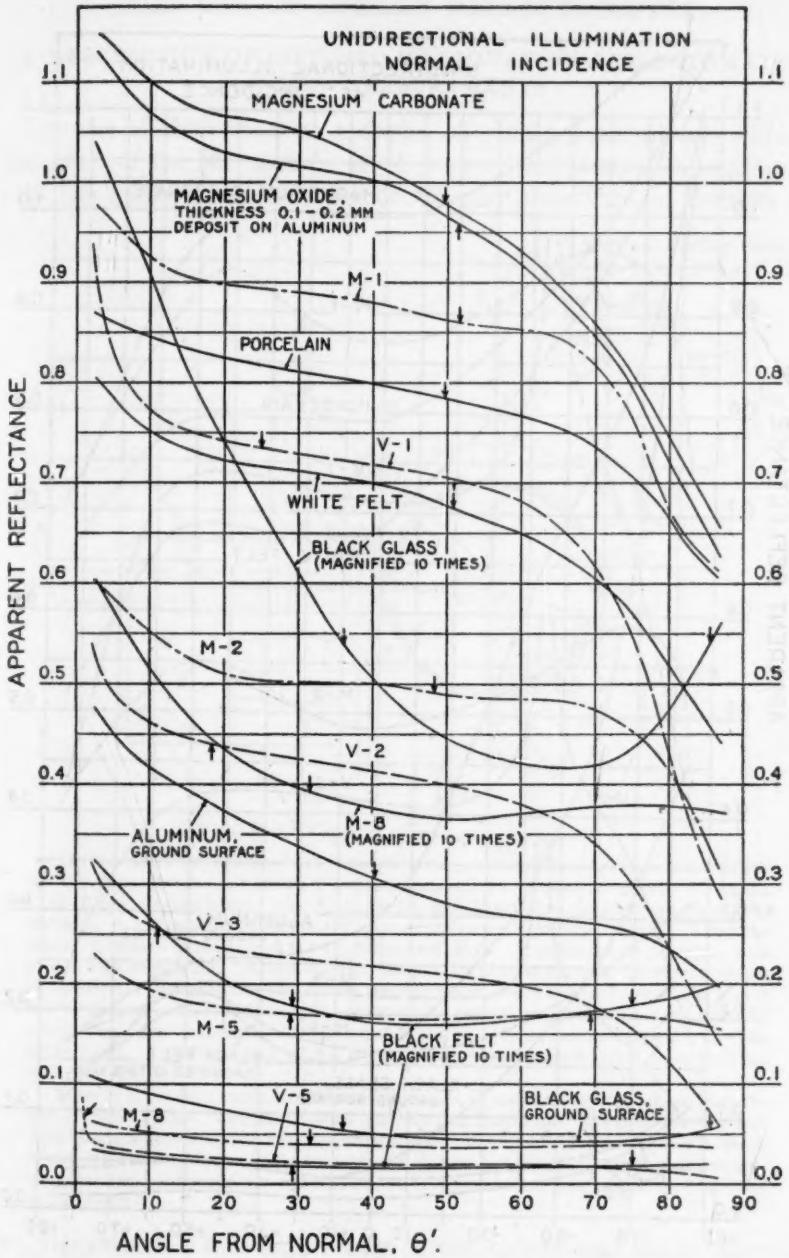

FIG. 6.—*Apparent reflectances for unidirectional normal illumination*

Vertical arrows on curves mark angles of observation for which the apparent reflectance is equal to the reflectance. (Reciprocal interpretation of curves: Apparent reflectances for normal observation and various angles of unidirectional illumination.)

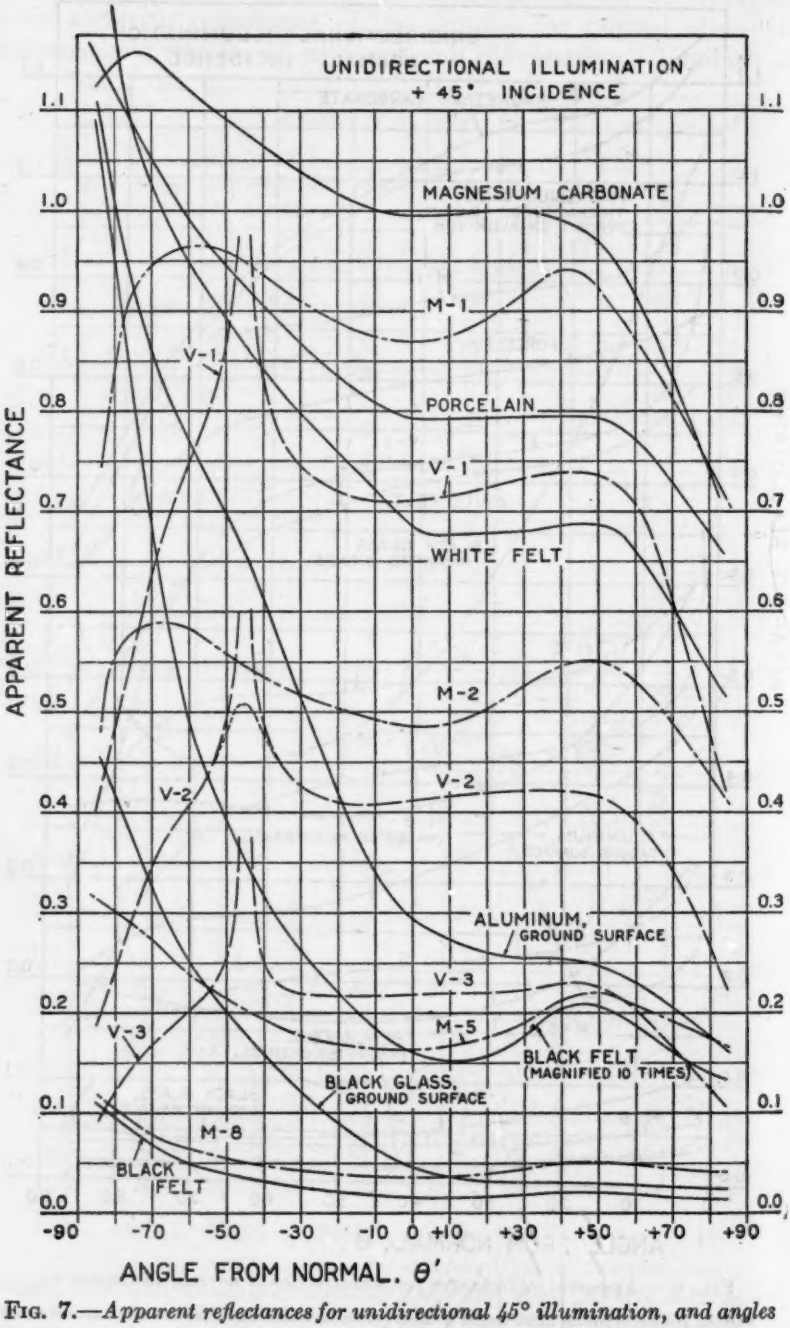

FIG. 7.—*Apparent reflectances for unidirectional 45° illumination, and angles of observation in the plane of incidence*

(Reciprocal interpretation: Apparent reflectances for 45° observation and unidirectional illumination at angles in the plane of observation.)

VIII. USE OF SPHERE REFLECTOMETER

1. DESCRIPTION OF DIFFUSED-ILLUMINATION REFLECTOMETER AND MEASUREMENTS

The use of the sphere as a device to obtain a completely diffused illumination on the sample is of particular interest in connection with the general method of reflectometry described in Section IV.

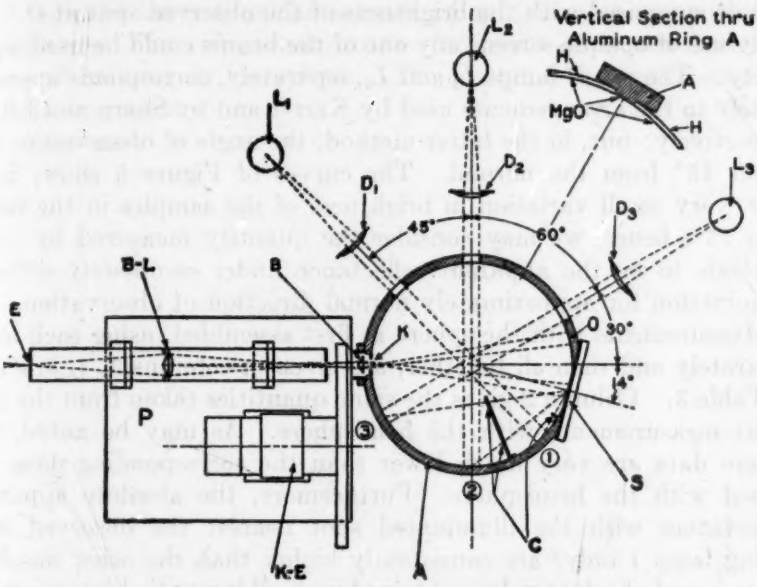

FIG. 8.—*Diagram of sphere reflectometer*

A, horizontal section through center of aluminum ring, 20 cm inside diameter, which supports two iron hemispheres. *S*, position of sample; opening 2 cm square into sphere. L_1, L_2, L_3, 9 volt 27 c. p. Mazda lamps. D_1, D_2, D_3, lenses, each 10 diopters, placed 12 cm from lamp filaments. *1*, *2*, *3*, position of illuminated spots on sphere wall; size approximately 15 mm diameter. *C*, screens to shade sample from illuminated spots. *P*, photometric apparatus; same as used with hemisphere. *See also* Figure 2. *O*, position of observed spot. *K*, aperture 6 mm in diameter. Other apertures into sphere, through which beams 1, 2, and 3 enter, are each 15 mm in diameter. *B*, biprism used to obtain greater separation between observed spot and sample than would be obtained with biprism at *B-L* alone. These prisms were taken from material on hand. A single biprism at *B-L* of the proper refracting angle would accomplish the same purpose.

The center of the illuminated and observed spots, and all apertures into the sphere, lie in the same horizontal plane. To obtain a small intensely illuminated spot with small aperture into the sphere, a projection system with condenser and objective lenses should be used. The above simple arrangement has served the purpose well enough, but the illumination on the sample (using one lamp only) was not sufficient for the best photometric precision in the brightness measurements.

For this reason a thorough study of the sphere was made, showing the effect of the departure of the reflective properties of the wall from the theoretical conditions previously assumed.

A sphere was built up of two iron hemispheres fitted into a metal ring *A* (fig. 8). A horizontal section through center of the ring *A*, light sources, and sample is shown in the figure. The interior of the sphere was first coated with aluminum paint and then covered

with a deposit of magnesium oxide. Three beams of light were projected into the sphere, forming the directly illuminated spots at positions 1, 2, and 3. These spot sources are shaded from the sample by screens C and situated at angular distances of 60, 38, and 8°, respectively, from the normal to the observed spot at O. The same photometric apparatus P, previously used with the hemisphere (fig. 3), could be transferred to the sphere, and the brightness of the sample compared with the brightness of the observed spot at O.

By use of opaque screens any one of the beams could be used separately. The use of lamps L_1 and L_2, separately, corresponds approximately to the arrangements used by Karrer and by Sharp and Little, respectively; but, in the latter method, the angle of observation was about 15° from the normal. The curves of Figure 5 show, however, very small variation in brightness of the samples in the range 0 to 15°; hence, we may consider the quantity measured by these methods to be the apparent reflectance under completely diffused illumination for approximately normal direction of observation.

Measurements with the sphere as first assembled, using each lamp separately and then all together, are given in columns 3, 4, 5, and 6 of Table 3. Column 2 gives the same quantities taken from the previous measurements with the hemisphere. As may be noted, the sphere data are very much lower than the corresponding data obtained with the hemisphere. Furthermore, the absolute apparent reflectances with the illuminated spot nearest the observed spot (using lamp 1 only) are consistently higher than the other absolute values; and absolute values obtained with all lamps lie between those for lamps 1 and 2, respectively. The use of all lamps together tends to give a more uniform distribution of brightness over the sphere wall and to eliminate the effect of the position of the illuminated spot.

After these measurements were made it was noticed that the lower half of the sphere and central ring appeared just perceptibly brighter than the upper hemisphere. The lower hemisphere and central ring had been coated as a unit with magnesium oxide and had, apparently, received a heavier deposit than the upper hemisphere, so that a considerable difference probably existed between the reflectances of the two parts. The upper hemisphere was consequently removed and given an additional deposit of oxide. This operation did not alter the diffuse reflective properties of the illuminated or observed spot, since they are all located on the central ring. To the unaided eye, placed at the sample opening, the interior of the sphere now appeared to be of uniform brightness.

The result was a marked increase in the numbers found for the absolute apparent reflectances. Measurements on samples M–1, V–1, porcelain, and magnesium carbonate, showed decreasing values (as

in previous case) for lamps 1, 2, and 3, used separately; but the extreme differences (between lamps 1 and 3) were reduced approximately 30 per cent. The average difference between values for lamps 1 and 3 was now only 3 per cent. The data for all samples, using all lamps together, are given in column 7 of Table 3. These values are very nearly equal (within 1 per cent) to the absolute values obtained with lamp 2 used alone (after recoating the upper hemisphere), but are 6 per cent lower than the corresponding data obtained with the hemisphere. These discrepancies are the result of incorrect conditions still existing in the sphere. The matter is fully discussed in the following section.

TABLE 3.—*Measurements of apparent reflectance, A_D (7), with sphere reflectometer*

Sample	Hemispherical source; data taken from Figure 5	First set of measurements with sphere, showing effect of incorrect conditions existing in sphere				Date obtained with sphere, after improving conditions by additional deposit of MgO; all lamps used		Apparent reflectance of samples relative to that of the porcelain sample taken as unity; calculated from data in columns 2, 3, 4, 5, 6, and 7					
		Lamp No. 1	Lamp No. 2	Lamp No. 3	All lamps	Observed	Corrected by factor 1.06 [1]						
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Matt papers:													
M-1	0.858	0.806	0.780	0.771	0.788	0.813	0.862	1.091	1.056	1.061	1.064	1.067	1.100
M-2	.495	.473	.457	.450	.462	.465	.493	.628	.620	.622	.621	.626	.629
M-5	.170	.164	.159	.160	.162	.164	.174	.216	.215	.216	.221	.219	.222
M-8	.038					.0375	.040	.048					.061
Glossy papers:													
V-1	.736	.696	.675	.663	.678	.695	.736	.935	.912	.918	.914	.919	.939
V-2	.437	.415	.408	.400	.409	.413	.437	.556	.544	.555	.552	.554	.558
V-3	.254	.234	.230	.226	.231	.226	.240	.323	.307	.313	.312	.313	.306
V-5	.062					.0575	.061	.079					.078
Magnesium carbonate	.961	.927	.900	.888	.905	.927	.983	1.247	1.215	1.225	1.225	1.226	1.253
Porcelain	.787	.763	.735	.725	.738	.740	.784	1.000	1.000	1.000	1.000	1.000	1.000
White felt	.667	.643	.624	.618	.629	.634	.672	.847	.843	.849	.852	.852	.857
Black felt	.017					.0181	.019	.021					.024
Aluminum (ground surface)	.304					.287	.304	.386					.398
Black glass:													
Ground surface	.054					.0529	.056	.069					.071
Polished surface	.043					.0406	.043	.055					.055
Silvered-glass mirror	.830	.647	.632	.698	.698	.764	.810	1.054	.848	.860	.963	.946	1.033

[1] The factor 1.06 is the ratio of the brightness of the observed spot on the sphere wall to the "equivalent-hemisphere" brightness of the spherical source. It is a factor belonging to the sphere and insuring a correct evaluation of the total illumination on the sample by means of a single observation of the brightness of the sphere wall. (See full explanation in text.)

2. EVALUATION OF ILLUMINATION ON SAMPLE

The differences between the apparent reflectances obtained with the sphere and hemisphere may be explained by the departure of the sphere wall from the theoretical conditions previously assumed. The unfulfilled conditions are (1) the departure of the sphere wall from a perfect diffusor, and (2) the variation of the reflectance over different parts of the sphere.

They are not independent in their effect on the measurements. The first defect causes variations in the brightness of the observed spot (and other parts of the sphere wall) corresponding to different positions of the illuminated spot. The magnitude of these variations depends also on the second defect but decreases as the average reflectance of the wall increases. If the sphere wall is a perfect diffusor but of varying reflectance, the position of the illuminated spot has no effect whatever on the brightness distribution over the sphere or on the measurements of apparent reflectance. The second defect causes a constant error in the measurement of the apparent reflectance for all samples. This error varies with the first defect, but exists even when the sphere wall is a perfect diffusor. The relative magnitude of these effects and the possibility of their elimination will now be considered in connection with the experimental data.

As a consequence of the departure of the sphere wall from a perfect diffusor, the brightness of the observed spot (hence the apparent reflectance of a sample) varies with the position of the illuminated spot. The relative brightnesses of the observed spot, when lamps L_1, L_2, and L_3 are used separately, can be determined approximately from the construction of the sphere reflectometer (fig. 8), the geometry and properties of the sphere itself, and the reflective properties of the magnesium oxide surface.

Measurements on films of magnesium oxide[26] deposited on aluminum have been made with the equipment herein described. Data for unidirectional normal illumination are given in Figure 6. In the following discussion the ordinates of this curve are taken to represent the relative brightnesses of an illuminated spot on the sphere wall—even though the thicknesses and reflectances of the oxide layer may be different in the two cases. Brightness measurements for completely diffused illumination were made on a film approximately 0.3 mm thick deposited on aluminum. The brightness was found to remain constant for various angles of view (as in the case of magnesium carbonate), and the measurements show that a sufficiently thick layer

[26] In the selection of samples for this investigation only materials likely to remain permanent in their reflective properties were chosen. It is known that the reflectance of a magnesium oxide film varies with the thickness of deposit and, for thin layers, with the reflectance of the material upon which it is deposited. The film is also very fragile and of questionable permanence in reflective properties. For these reasons, and because a magnesium carbonate block served equally well as a good diffusor of high reflectance, a magnesium oxide sample was not included in the regular series of measurements (which have extended over a period of several months).

of the oxide has a very high reflectance, practically the same as that found for the carbonate.

The following steps may be noted in the determination of the effect of the position of the illuminated spot:

1. The brightness of the observed spot is always compared in the photometer with the brightness of another part of the sphere wall (occupied by a sample). Consequently, the relative brightnesses (photometer readings) of the observed spot, when lamps L_1, L_2, and L_3 are used separately, do not depend on the constancy or total quantity of the light projected into the sphere from each lamp. Furthermore, the light from each lamp is incident normally on the sphere wall and is diffusely reflected in the same manner from each illuminated spot. Hence, for the purpose in view, the spot sources 1, 2, and 3 may be regarded as equal in all respects.

2. The total illumination E of the observed spot, due to either of the spot sources 1, 2, or 3, used separately, may be divided into three components:

$$E = E_a + E_b + E_c$$

where E_a is received directly from the illuminated spot, E_b is contributed by the first reflection of the direct illumination of all other parts of the sphere, and E_c results from the multiple reflections of E_b.

3. The difference in brightness of the observed spot, when viewed normal to its surface and nearly normal (as in fig. 8), is assumed to be negligible for each of the three components of illumination.

4. Lines connecting the spot sources 1, 2, and 3 with the observed spot at O (fig. 8) make angles of 60, 38, and 8°, respectively, with the normal at O, and also make the same angles with the corresponding normals to the spot sources.

5. From the geometry of the sphere the illumination of the observed spot, due to the component E_a from either of the spot sources 1, 2, or 3 is independent of the distance of this source from the observed spot.

6. Owing to the departure of the magnesium oxide surface from a perfect diffusor (for unidirectional normal illumination), the direct illumination of the observed spot is different, however, for sources 1, 2, or 3, and proportional to the ordinates of the curve (in fig. 6) for angles 60, 38, and 8°, respectively. Recalling the reciprocal interpretation of the curves in Figure 6, it is evident that the normal brightnesses of the observed spot, due to spot sources 1, 2, and 3, used separately, are in the proportion $(0.916)^2 : (1.005)^2 : (1.083)^2$, respectively.

If the magnesium oxide surface were a perfect diffusor with the same reflectance for unidirectional normal illumination, these brightnesses would be the same in all three cases and, on the same brightness scale, would have the value $(0.957)^2$, where 0.957 is the mean ordinate of the curve for magnesium oxide.

7. It has been shown by others [27] (assuming perfect diffusion in the sphere) that

$$\frac{E_a}{E}=1-R$$

where R is the average reflectance of the sphere wall. By inspection of the interior surface of the sphere wall and comparison with the deposit of magnesium oxide measured (fig. 6), an estimate of 0.92 for the average reflectance of the sphere wall seemed reasonable. Then the component E_a is 8 per cent of the total illumination.

8. The magnitude of the second component is given by

$$\frac{E_b}{E-E_a}=1-R$$

or

$$\frac{E_b}{E}=(1-R)\,R=0.074$$

The second component is shown to be small and, while not completely diffused, is incident on both sample and observed spot. Compared with the first component its effect on the relative brightnesses is certainly negligible. Components E_b and E_c together represent 92 per cent of the total illumination of the observed spot and may be regarded here as completely diffused.

9. The experimental data on magnesium oxide for completely diffused illumination show that its brightness does not vary appreciably with the angle of view. Consequently, the sphere wall acts as a perfect diffusor for the components E_b and E_c, and the reflectance is the same for both unidirectional and diffused illumination.

Adding 8 per cent of the brightness due to component E_a alone to 92 per cent of the brightness E_a would give if the sphere wall acted as a perfect diffusor for this component (as it does for components E_b and E_c), the relative brightnesses of the observed spot, due to the total illumination received from spot sources 1, 2, and 3, used separately, are found to be in the proportion (0.910):(0.924):(0.937).

The above determination is not presumed to be accurate. It is a probable explanation, however, of some of the experimental results, for it is evident from the definition of the apparent reflectance that these calculated differences in the brightness of the observed spot will account for the observed difference of 3 per cent between the absolute apparent reflectances measured with lamps 1, 2, and 3, used separately (after the additional deposit of magnesium oxide had been made). The calculations and observations show that the position of the illuminated spot relative to that of the observed spot may have an appreciable effect on the measurements with the sphere when the

[27] See footnote 16.

average reflectance of the sphere wall is not very high. Although it is impossible to make the sphere wall a perfect diffusor for all types of illumination, it is possible to make the average reflectance high enough to render the effect negligible. The additional deposits of magnesium oxide, referred to in the description of the experiments with the sphere, made the reflectance of the sphere wall more uniform over all its parts and increased its average value. The component E_a was unaltered, E_b was increased slightly, but E_c was increased very much more, thus decreasing the effect of the relative positions of the illuminated and observed spots.

Consider, now, the effect due primarily to the nonuniform reflectance over the sphere wall. The brightness distribution over the sphere depends directly on the reflectance of the various parts as well as on the diffusing properties of the wall. In the use of the sphere the brightness of the observed spot is taken as a measure of the illumination on the sample. Obviously, then, this brightness (observed from the position of the photometer) must be equal to the equivalent-hemisphere brightness of the spherical source (as viewed from the sample), otherwise the measurements will be in error by a constant factor for all samples. The approximately constant difference observed between the sphere data and the hemisphere data (Table 3, columns 7 and 2) suggests that this incorrect condition may exist in the sphere reflectometer herein described. The ratio of the equivalent-hemisphere brightness of the sphere to the brightness of the observed spot was directly determined (for the case of all lamps) by the same procedure followed previously with the hemispherical source.

Using a mirror of known reflectance, the brightness at various points on the sphere wall relative to the brightness of the observed spot was measured with the photometer, sets of measurements being made at angles of approximately 10, 20, 30, 40, and 60°, respectively, from the normal to the plane of the sample holder. It may be noted that in this way only little more than half of the sphere wall opposite the sample was covered. However, the region in the neighborhood of 45° is most effective in determining the illumination on the sample. This fact is indicated by the large value which the factor $K(\theta)$ (see equations (17) and (18)) takes for angles in this region. In the case of the hemisphere these results are the combined (opposing) effects of two physical conditions—first, the increase in area of zones as θ increases, and, second, the decrease in component of illumination from each zone which results from the approach to grazing incidence. In the case of the sphere there is the further complication of variation in distance from the several elements of the sphere wall, but the general effect is the same in that the zones in the neighborhood of 45° remain most effective.

Using equation (17), a value of 0.94 was obtained from these measurements, showing that the brightness of the observed spot [28] was 6 per cent higher than the equivalent-hemisphere brightness of the whole sphere. The directly measured brightness ratios in Table 3, column 7, were then corrected by a factor 1.06, which thus completely eliminates the error in the evaluation of the total illumination on the sample resulting from a nonuniform brightness distribution over the sphere wall. The corrected values are tabulated in Table 3, column 8, and Table 2, column 7, and are in good agreement with the corresponding data obtained by the other methods (compare with Table 2, columns 3 and 11).

It is of interest to compare the relative apparent reflectances of the samples, as expressed in terms of the apparent reflectance of the porcelain sample (chosen arbitrarily), and measured under the different approximations to completely diffused illumination and normal observation obtained with the sphere and hemisphere. These data are given in the last six columns of Table 3. The general agreement of values for all samples (excepting the mirror samples) shows that the difference between the brightness of the observed spot and the equivalent-hemisphere brightness of the entire sphere wall is a greater source of error than any change in the normal brightness of the sample resulting from the corresponding variation in the angular distribution of the incident light from the ideal completely diffused type of illumination. Hence, for relative apparent reflectance measurements, the illumination in all these cases seems to be a sufficient approximation to complete diffusion for practical purposes. To make absolute measurements, however, one must be assured that the brightness of the observed spot is a correct measure of the total illumination on the sample.

If the variations from the ideal conditions desired in the sphere are not too large, then the total effect (again excepting the mirror samples) may be expressed by the ratio of the brightness of the observed spot to the equivalent-hemisphere brightness of the sphere. This ratio is a correction factor belonging to the sphere reflectometer and insuring a correct evaluation of the illumination on the sample by means of a single observation of the brightness of the sphere wall.

3. ERRORS IN MEASUREMENT OF REFLECTED LIGHT

In the case of the mirror samples and samples having a fairly distinct specular component of reflectance with little or no diffuse component, the correction factor above determined may cease to

[28] An examination of the interior of the sphere after the measurements were completed showed a thicker deposit of the oxide in the region of the observed spot than over the greater part of the remaining surface; hence, the reflectance may be appreciably higher in this region. The effect of the departure of the magnesium oxide from the perfect diffusor will also result in a slightly higher illumination on the central ring opposite the directly illuminated spots. These observations are in qualitative agreement with the results of the brightness distribution measurements.

cover adequately the total effect of the departure of the sphere wall from the desired conditions. The illumination may not be a sufficient approximation to complete diffusion for these samples. Only a very limited region of the source contributes to the light reflected into the photometer, and if the brightness of this region is not equal to the equivalent-hemisphere brightness of the source another correction factor must be applied, which is the ratio of the equivalent-hemisphere brightness of the source to the brightness of that area of the source actually used. This second correction factor reduces the evaluation of the reflected light (as given by the photometer) to the value which would be obtained if the illumination on the sample were completely diffused. This correction was not applied to the data in Table 3.

The two correction factors defined may obviously be combined into a single factor (for mirror samples) which is the ratio of the brightness of the observed spot to the brightness of that part of the sphere source actually contributing to the light entering the photometer.

Assuming, again, that all theoretical conditions affecting the angular distribution of the incident luminous flux and its correct evaluation have been satisfactorily realized, the variation in brightness of the sample for different angles of view remains as a source of error in the evaluation of the *total reflected flux*—by means of a single brightness measurement of the sample.

An approximation to the true reflectance for completely diffused illumination is obtained, however, by observing the sample at an angle of approximately 55 or 60° from the normal. The degree of approximation obtained is shown in columns 9 and 10 of Table 2. These data give the errors to be expected in the use of this type of reflectometer (for the measurement of R_D), due entirely to the mixed specular and diffuse reflection characteristics of the samples.

The proper choice of the angle of observation is thus seen to be of prime importance; but, unfortunately, there is no one angle suitable for all samples and apparently no simple correction which may be readily applied to eliminate the effect.

4. DESIGN OF SPHERE

A properly designed sphere may, nevertheless, be of considerable use for many purposes. The data obtained suggest a design such as sketched in Figure 9. This sphere may be conveniently built up as shown in Figure 8, but first coated on the inner surface with a thick layer of white porcelain enamel (baked) and then smoked heavily with magnesium oxide. A surface of uniformly high reflectance would be obtained in this way.

The illuminated spot is located opposite the observed spot, and the beam of light is incident at approximately 50°. For this angle of

incidence the first reflected light from the illuminated spot to the observed spot and thence to the photometer is approximately the same as it would be if the sphere wall were actually a perfect diffusor. The multiply reflected light, incident on both observed spot and sample, may be regarded as completely diffused.

The angle of observation may be varied over a range from 50 to 60° (or more) by rotating the photometer (or the sphere) about an axis through the sample. The position of the observed spot and the angle at which it is viewed would vary somewhat, but the reflective properties of magnesium oxide are such that this variation would cause no appreciable change in the brightness of the observed spot.

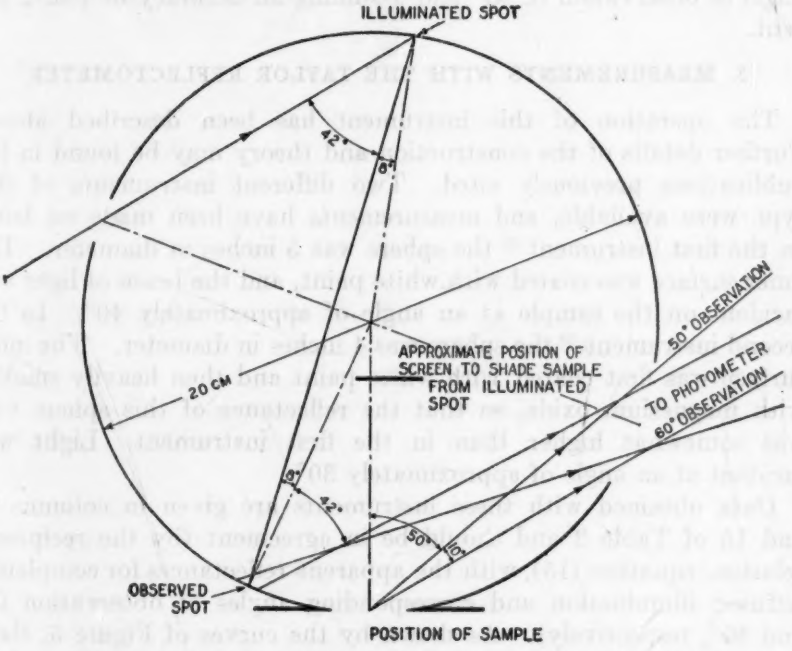

FIG. 9.—*Suggested design of sphere*

With this arrangement, the screen used to shade the sample from the illuminated spot will subtend a rather large angle at the sample. Care should be taken to make this screen of highly reflecting material, so that its brightness (as viewed from the sample) does not differ greatly from the brightness of the sphere wall. This is the essential condition to be fulfilled. The screen need not be opaque; a translucent screen, such as milk glass, of proper thickness, so that its brightness exactly matches the brightness of the sphere background, could be used. The openings into the sphere for the entrant and emergent beams of light would amount to about 1 per cent of the whole sphere surface.

With this construction, it is believed that the error made in the evaluation of the total illumination on the sample would be very small if not negligible. Remaining imperfections, if they exist, could be fully compensated by correction factors, determined for the sphere as described above. Measurements on a sample over the range from 50 to 60° would give some indication as to the uncertainty of the determination of the reflectance R_D, and with some previous knowledge of the reflection characteristics of the sample this range of uncertainty could be narrowed by proper choice of the angle of observation. Thus, for matt samples of the kind herein studied (of not extremely low reflectance), one would be quite safe in choosing an angle of observation of 55° and assuming an accuracy of 1 or 2 per cent.

5. MEASUREMENTS WITH THE TAYLOR REFLECTOMETER

The operation of this instrument has been described above. Further details of the construction and theory may be found in the publications previously cited. Two different instruments of this type were available, and measurements have been made on both. In the first instrument [29] the sphere was 5 inches in diameter. The inner surface was coated with white paint, and the beam of light was incident on the sample at an angle of approximately 40°. In the second instrument [30] the sphere was 4 inches in diameter. The inner surface was first coated with white paint and then heavily smoked with magnesium oxide, so that the reflectance of this sphere wall was somewhat higher than in the first instrument. Light was incident at an angle of approximately 30°.

Data obtained with these instruments are given in columns 14 and 15 of Table 2 and should be in agreement (by the reciprocal relation, equation (15), with the apparent reflectances for completely diffused illumination and corresponding angles of observation (40 and 30°, respectively). As shown by the curves of Figure 5, there is very little difference between the data for 40 and 30°. The values for 35° are recorded in column 4 of Table 2 and are in good agreement with the sphere data—for samples of medium and high reflectance. Both instruments give definitely higher values, however, for samples of low reflectance.

An analysis of the performance of this type of reflectometer is not contemplated here. It may be noted, however, that in both instruments, when the entering beam is projected on the sphere wall,

[29] This was the original instrument described by Taylor (loc. cit.) and located in the photometric laboratory of the Bureau of Standards. In the present work a Weber photometer was used for the brightness measurements instead of the Macbeth illuminometer, as described in the publications cited.

[30] This instrument was the property of the Research Laboratory of the Munsell Color Co., Baltimore, Md., and kindly placed at the disposal of the writer for these measurements by the director of the laboratory. The photometric equipment consisted, essentially, of a flicker disk and milk glass diffusing screen, the brightness of which could be controlled by varying the distance of a lamp from the screen.

the brightness of the observed spot varies appreciably with the position of the illuminated spot on the wall and with the reflectance of the sample itself, which occupies about 2.5 per cent of the sphere surface in the first instrument and 3.2 per cent in the second instrument.

A greater part of the apparatus used in this investigation was constructed in the physical laboratory shop of the Johns Hopkins University, the remainder in the shops of the Bureau of Standards. The writer wishes to express his appreciation of the help thereby extended by Professor Ames. The work was done at the Bureau of Standards as part of its research program in colorimetry.

WASHINGTON, October 29, 1927.

INTERFEROMETER MEASUREMENTS OF WAVE LENGTHS IN THE VACUUM ARC SPECTRA OF TITANIUM AND OTHER ELEMENTS

By C. C. Kiess

ABSTRACT

Wave-length determinations by means of the Fabry-Perot interferometer have been made for the vacuum arc spectrum of titanium. More than 300 lines have been measured between 6743 A in the red and 2941 A in the ultra-violet. For many of the lines the accuracy of measurement exceeds 1 part in 6,000,000; for the majority it exceeds 1 part in 4,500,000. Using only the wave numbers of lines of wave lengths longer than 4700 A, and constant wave-number differences as determined in various parts of the spectrum, a set of terms has been derived, which have been used to calculate the wave lengths of the blue and violet lines. The comparison of calculated with observed wave lengths indicates that no difference in scale exists between the red and violet regions. In addition to titanium some wave lengths were measured for iron, copper, calcium, barium, and other elements.

CONTENTS

	Page
I. Introduction	75
II. Method of observation	76
III. Results for titanium	77
1. Description of Bureau of Standards wave lengths	77
2. Comparison with other observations	84
3. Computation of wave lengths from spectral terms	84
IV. Results for other elements	86
1. Iron	88
2. Copper	89
3. Na, Al, Ca, V, Cr, Mn, Ni, Ba	90
V. Acknowledgments	90

I. INTRODUCTION

In the summer of 1923 the Allegheny Observatory and the spectroscopy section of the Bureau of Standards entered upon a cooperative program for the determination of standard solar wave lengths by interference methods. The results of that work, wave lengths of more than 700 Fraunhofer lines included between 3592 and 7148 A, have now been published.[1] From the earlier results of the solar work it became apparent that a comparison of solar with laboratory wave lengths would have significance only if the latter were obtained from sources unaffected by conditions not present in the sun. It was,

[1] Publ. Allegheny Observatory, **6**, p. 105; 1926; pp. 125 and 141; 1927.

therefore, decided to enlarge the scope of the program to include the determination of the vacuum arc wave lengths of the more prominent elements appearing in the solar spectrum.

In the present paper are given the results which have been obtained for the element titanium from 6743 A in the red to 2941 A in the ultra-violet. Some wave lengths of other elements were also measured during the course of the work, and these are presented at this time because of their significance for the solar problem.

II. METHOD OF OBSERVATION

Light rays from the vacuum arc and from the neon tube, which served as the source of standards, were delivered simultaneously to the Fabry-Perot interferometer. The vacuum arc was identical with that designed and described by Curtis.[2] The beam from the arc, perpendicular to the line joining the Ne tube and the slit of the spectrograph, was collimated with the beam from the Ne lamp by means of a thinly silvered diagonal mirror placed about 20 cm in front of the interferometer. The arrangement of the sources was in all respects similar to that used previously in the redetermination of secondary standards from the iron arc.[3]

The material used in the arc was powdered titanium carbide which was packed into a cored graphite rod that served as the lower and positive electrode. The upper, negative electrode was usually a copper rod, but for a few exposures, an upper graphite electrode was employed. The arc operated at 240 volts, d. c. and 8 amperes, and was struck when the bell surrounding it was partially exhausted. When the chamber was reduced to about 10 mm Hg pressure, as indicated by a vacuum gauge, the arc burned steadily for periods approximating an hour without renewal or readjustment of the electrodes. When exposures were in progress the electrodes were separated by 1 cm, and the image projected onto the diaphragm of the interferometer was enlarged about 2.5 times.

Three series of observations were made in all. The first two were obtained with glass interferometer plates with Ag films cathodically deposited. For these two series a glass achromat was used to project the light from the interferometer onto the slit of the spectrograph. Invar etalons of 5, 7.5, 12, 15, 20, and 25 mm thickness were used to separate the plates. In the first series of observations the small camera which takes a flat plate 6 by 20 cm was used. The region covered was from 5500 to 7500 A. In the second and third series of observations the large camera was used. This takes a thin plate 6 by 40 cm, which can be bent over a template to fit the

[2] J. Opt. Soc. Am. and Rev. Sci. Inst., 8, p. 697; 1924.
[3] B. S. Sci. Papers, No. 478, 19, p. 263; 1924.

focal curve of the grating. The second set of observations extended from 3650 to 6550 A, and the third from 2820 to 6550 A. The interferometer plates used for the third set were of crystalline quartz and were thinly sputtered with Pt films, and for projecting the rings it was necessary to use the quartz-fluorite achromat. Etalons of 3, 5, 6, 7.5, 8, 12, 15, and 20 mm were used as separators for the quartz plates.

The spectrograph used for all the work was the one carrying the 7,500-lines per inch Anderson concave grating. It has been described elsewhere.[4] The first series of observations was obtained on Eastman 33 plates sensitized with pinacyanol. For the second and third series either experimental plates prepared in the bureau's emulsion laboratory or Schleussner ultrarapid plates were used. Half of each long plate was panchromatized by bathing in a mixture of pantochrome and pinacyanol for recording the green, yellow, and red rays.

For the first series of plates the method of reduction employed in previous work was followed.[5] For the second and third series, however, a slight modification of that described by Robertson[6] or by Childs[7] was adopted. A similar procedure was adopted for the reduction of some of the solar observations mentioned above.[8]

III. RESULTS FOR TITANIUM

1. DESCRIPTION OF BUREAU OF STANDARDS WAVE LENGTHS

Table 1 contains the wave lengths which have been measured in the vacuum arc spectrum of titanium in terms of the neon standards. The values of the Ne lines used for finding the interferometer thicknesses are those of Burns, Meggers, and Merrill.[9] The justification for using these lines as standards instead of the primary standard, the red ray of cadmium, lies not only in the ease and economy with which they may be produced, but also in the fact that in the determination of secondary standards in spectra where exceedingly high orders of interference are not possible, they lead to results of the same precision as is obtained with the use of the Cd standard. This is demonstrated by the recent work of Babcock[10] on the iron spectrum.

The wave lengths entered in the first column of Table 1 are the means of the individual results derived from all the plates. These values are for air at 15° C. and 760 mm Hg pressure. The results

[4] B. S. Sci. Papers, Nos. 312, 441, and 499.
[5] B. S. Sci. Papers, Nos. 251, 274, 302, 327, 329, 441, 478, and 479.
[6] J. Opt. Soc. Am. and Rev. Sci. Inst., **9**, p. 611; 1924.
[7] J. Sci. Inst., **3**, pp. 97 and 129; 1926.
[8] Publ. Allegheny Observatory, **6**, p. 126; 1927.
[9] B. S. Sci. Paper No. 329, **14**, p. 765; 1918.
[10] Astrophys. J., **66**, p. 256; 1927.

from the Ag films required correction for dispersion of phase change which was determined by the method of short and long etalons as described by Meggers.[11] The phase change curve is illustrated in Figure 1. No phase change correction was apparent for the results obtained with the Pt films in the region under investigation. However, when the means of the wave lengths obtained with the Pt films were compared with the means of all the observations, it was found that they were systematically higher by 0.001 A from 5150 to 4850 A by 0.002 A from 4850 to 4070 A; and by 0.003 A from 4070 to 3650 A. Accordingly, the wave lengths in Table 1 which were derived only from the Pt films have been corrected by the above amounts, the

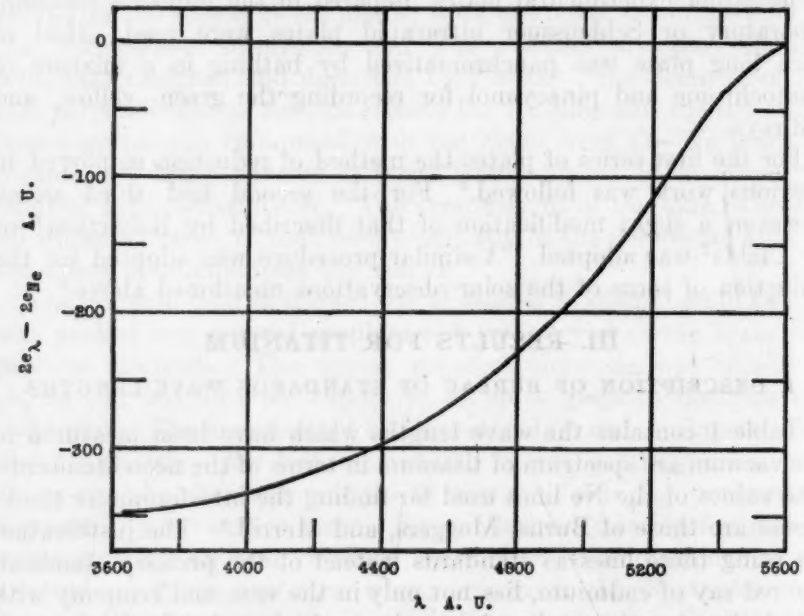

FIG. 1.—*Dispersion of phase change at reflection from silver films*

correction 0.003 A being extrapolated to apply to all the lines shorter than 3650 A. The justification for this procedure is given below in the discussion on the calculation of wave lengths from spectral terms.

In columns 2 and 3 of Table 1 are entered the number of observations from which the mean values of the wave lengths were derived, and letters indicating the probable errors of the determinations. The probable errors are expressed in parts per million; thus the letter A denotes a p. e. of 1 part in 6,000,000; B, 1 part in 4,500,000; C, 1 part in 3,000,000; and D, probable errors greater than 1 in 3,000,000. The fourth column of the table contains the intensities and temperature classes of the lines as determined by King.[12] Lines emitted

[11] B. S. Sci. Papers No. 251, **12**, p. 199; 1915.
[12] Astrophys. J., **39**, p. 139; 1914; **59**, p. 155; 1924.

by the ionized Ti atom are designated in this column by the symbol Ti II. The remaining three columns of the table contain data the significance of which is discussed below.

TABLE 1.—*Vacuum arc wave lengths of titanium*

λ I. A.	Number of observations	Weight	Intensity and temperature class	ν (Vac)	Term combination	(O−C) λ
6743.124	6	A	10 III*A*	14825.836	$aD'-aD$	
6556.066	17	A	25 III	15248.847	$b^3F_4-d^3F'_4$	000
6554.226	16	A	30 III	15253.126	$b^3F_3-d^3F'_3$	000
6546.276	12	A	20 III	15271.650	$b^3F_2-d^3F'_2$	000
6366.354	6	C	8 III	15703.246	$b^3F_4-c^3D_3$	+004
6336.104	2	D	8 III	15778.216	$b^3F_3-c^3D_2$	000
6312.240	6	C	10 III	15837.866	$b^3F_4-b^3G_4$	+003
6303.754	6	C	10 III	15859.188	$b^3F_3-b^3G_3$	+010
6261.101	26	A	35 II	15967.225	$b^3F_2-b^3G_3$	−001
6258.706	23	A	50 II	15973.336	$b^3F_4-b^3G_5$	000
6258.103	24	A	40 II	15974.875	$b^3F_3-b^3G_4$	000
6126.217	16	A	20 II	16318.780	$a^3P_2-a^3S_1$	
6091.175	16	B	20 III	16412.662	$bG'-bG$	
6085.228	16	A	20 II	16428.700	$a^3P_1-a^3S_1$	
6064.631	3	B	9 II*A*	16484.496	$a^3P_0-a^3S_1$	
5999.668	1	D	8 III	16662.984	a^3H_4-bG	
5978.543	20	A	25 II	16721.863	$a^3G'_3-a^3H'_4$	000
5965.828	24	A	30 II	16757.501	$a^3G'_4-a^3H'_5$	000
5953.162	22	A	30 II	16793.155	$a^3G'_5-a^3H'_6$	000
5941.755	7	B	12 II*A*	16825.395	$a^3P_1-b^3D_1$	+005
5937.806	1	D	6 II*A*	16836.584	$a^3P_2-b^3D_2$	−002
5922.112	7	C	18 II	16881.201	$a^3P_0-b^3D_1$	+004
5918.548	2	D	10 II	16891.367	$a^3P_2-a^3P'_2$	
5903.317	1	D	5 III*A*	16934.947	$a^3P_2-a^3P'_1$	
5899.295	22	A	25 II	16946.493	$a^3P_1-b^3D_2$	000
5866.453	31	A	35 II	17041.364	$a^3P_2-b^3D_3$	+004
5804.265	8	C	5*n* IV	17223.947	$b^3G_4-c^3H_7$	
5785.979	3	B	5*n* IV	17278.379	$b^3G_5-c^3H_6$	
5774.037	6	C	5*n* IV	17314.116	$b^3G_4-c^3H_5$	
5766.330	3	D	4*n* IV	17337.257	$b^3G_3-c^3H_4$	
5739.464	5	B	9 III	17418.410	$a^3H_5-b^3H'_5$	000
5715.123	3	D	9 III	17492.594	$a^3H_6-b^3H'_6$	000
5689.465	7	B	10 III	17571.481	$a^3D_3-b^3F_3$	
5675.413	10	B	9 III*A*	17614.987	$a^3D_2-b^3F_4$	
5662.154	10	A	12 III	17656.237	$a^3D_4-b^3F_5$	
5648.570	4	D	5 IV	17698.695	$a^3D_3-c^3F_4$	+003
5644.137	13	A	18 III	17712.595	$bG'-cG$	
5565.476	11	A	9 III	17962.941	a^3H_4-cG	
5512.529	17	A	25 II	18135.471	$b^3F_4-e^3D_3$	+001
5503.897	8	B	8 III	18163.912	$aH-dG$	
5490.151	10	B	12 II	18209.391	$b^3F_4-b^1D_3$	
5488.210	2	D	5 III	18215.829	$a^3F'_3-c^3F_2$	000
5481.426	3	D	6 III	18238.374	$a^3F'_3-c^3F_3$	000
5477.695	11	B	8 III	18250.796	$a^3F'_4-c^3F_4$	000
5429.139	5	D	6 III	18414.022	$c^3P_2-d^3P'_2$	
5409.609	8	C	6 II	18480.500	$a^3G'_5-e^3F'_4$	−001
5397.093	5	D	4 III	18523.359	$a^3G'_4-e^3F'_3$	000
5389.996	2	D	3 III	18547.745	$a^3G'_3-e^3F'_2$	000
5369.635	3	D	4 III	18618.077		
5298.429	2	D	4 III	18868.284	$bD'-cP'$	
5297.236	3	D	6 III	18872.532	$a^3G'_3-f^3F'_3$	000
5295.781	2	D	4 III	18877.720	$a^3P_2-c^3D_3$	+002
5283.441	4	D	8 III	18921.809	$a^3G'_4-f^3F'_3$	000
5265.967	6	C	10 III	18984.597	$a^3G'_5-f^3F'_4$	+002
5224.928	3	D	8 III	19133.706	$a^3F'_4-b^5F_4$	

TABLE 1.—*Vacuum arc wave lengths of titanium*—Continued

λ I. A.	Number of observations	Weight	Intensity and temperature class	ν (Vac)	Term combination	(O−C) λ
5224.301	3	D	15 III	19136.006	$a^5F'_5-b^5F_5$	
5210.386	29	A	40 I	19187.107	$a^5F_4-a^3F'_4$	000
5192.971	26	A	35 I	19251.453	$a^5F_3-a^3F'_3$	−001
5173.742	27	A	30 I	19323.003	$a^5F_2-a^3F'_2$	000
5147.483	12	A	10 I*A*	19421.575	$a^5F_1-a^3F'_1$	+001
5145.465	13	A	12 II	19429.194	$b^5F_4-f^5D_3$	000
5120.420	10	A	12 III	19524.222		
5113.448	8	C	10 III	19550.843	$b^5F_3-f^5D_2$	000
5087.055	3	D	8 III	19652.277	$b^5F_2-f^5D_1$	000
5064.654	26	A	25 I	19739.198	$a^5F_4-a^5D_3$	000
5062.112	2	D	7 III	19749.111	$a^5D'_2-d^5P'_1$	000
5052.879	2	D	8 IV	19785.196	$a^5D'_3-d^5P'_2$	000
5039.959	22	A	22 I	19835.917	$a^5F_3-a^5D_3$	000
5038.400	15	A	25 II	19842.053	$b^5F_2-d^5G_3$	−001
5036.468	10	B	25 II	19849.667	$b^5F_3-d^5G_4$	000
5035.908	11	B	25 II	19851.873	$b^5F_4-d^5G_5$	+001
5025.570	9	C	18 III	19892.711	$a^5G_6-b^5F_5$	
5024.842	12	C	20 II	19895.592	$a^5F_5-b^5G_5$	
5022.871	22	A	25 II	19903.397	$a^5F_3-b^5G_3$	
5020.028	22	A	25 II	19914.670	$a^5F_4-b^5G_4$	
5016.162	19	A	20 II	19930.026	$a^5F_5-b^5G_6$	
5014.277	28	A	25 I	19937.512	$a^5F_1-b^5G_2$	
5014.185	3	D	25 I	19937.878	$a^5F_2-a^3D_1$	000
5009.652	1	D	7 I*A*	19955.917	$a^5F_3-a^3D_2$	+006
5007.209	28	A	40 II	19965.651	$a^5F_2-b^5G_3$	
4999.504	30	A	45 II	19996.425	$a^5F_3-b^5G_4$	
4997.099	2	D	8 I*A*	20006.046	$a^5F_3-a^3D_2$	+001
4991.067	30	A	50 II	20030.226	$a^5F_4-b^5G_5$	
4981.732	30	A	60 II	20067.757	$a^5F_5-b^5G_6$	
4978.191	8	C	10 III	20082.031	$a^5G_2-b^5F_1$	
4975.344	10	C	10 III	20093.523	$bD'-dF'$	
4938.283	9	D	8 IV	20244.321	$aH-fG$	
4928.342	13	A	12 III	20285.152	$a^3D'_1-g^3F'_2$	000
4921.768	13	B	12 III	20312.248	$a^3D'_2-g^3F'_3$	000
4919.867	11	B	10 III	20320.093	$a^3D'_3-g^3F'_3$	000
4913.616	20	A	20 III	20345.946	$a^3G'_3-b^3H'_4$	000
4899.910	24	A	20 III	20402.859	$a^3G'_4-b^3H'_5$	000
4885.082	25	A	20 II	20464.788	$a^3G'_5-b^3H'_6$	000
4870.129	15	A	20 III	20527.621	$a^3H_5-a^3I_6$	
4868.264	15	A	18 III	20535.483	$a^3H_4-a^3I_5$	
4856.012	19	A	20 III	20587.298	$a^3H_6-a^3I_7$	
4840.874	25	A	25 I	20651.676	$aD'-bD$	
4820.410	14	A	20 II	20739.345	$aG'-bF'$	
4805.416	13	B	12 III	20804.051	$c^3P_2-i^3D_3$	
4799.797	14	B	12 III	20828.412	$bG'-c^3H'_4$	
4792.482	13	A	10 III	20860.203	$c^3P_1-i^3D_2$	
4778.259	9	B	10 III	20922.292	a^3H_4-dG	
4759.272	21	A	25 III	21005.760	$a^3H_6-c^3H'_5$	
4758.120	18	A	25 III	21010.849	$a^3H_5-c^3H'_5$	
4742.791	18	A	20 III	21078.756	$a^3H_4-c^3H'_4$	
4731.172	7	A	9 III	21130.521	$a^3D'_3-h^3F'_4$	
4715.295	4	D	4 II*A*	21201.668	$a^3F_4-a^3G_4$	−005
4710.186	15	A	18 III	21224.663	$a^3P_0-c^3D_1$ / $a^3D'_3-h^3D_3$	
4698.766	21	A	20 II	21276.247	$a^3P_1-c^3D_2$	000
4691.336	24	A	20 II	21309.944	$a^3P_2-c^3D_3$	−001
4681.908	30	A	30 I	21352.857	$a^5F_4-a^3G_5$	+003
4675.118	9	C	10 III	21383.870	$a^3P_2-b^5D_3$	
4667.585	30	A	25 I	21418.381	$a^3F_3-a^3G_4$	+002
4656.468	30	A	25 I	21469.515	$a^3F_2-a^3G_3$	+005
4645.193	12	C	12 III	21521.626	$a^3P_1-c^3D_0$	
4629.336	24	A	15 III	21595.343	$a^3P_1-c^3D_2$	
4623.098	26	A	25 III	21624.478	$a^3P_2-c^3D_3$	
4617.269	29	A	30 II	21651.780	$a^3P_2-c^3D_4$	
4599.226	9	A	5 IV	21736.720		

TABLE 1.—*Vacuum arc wave lengths of titanium*—Continued

λ I. A.	Number of observations	Weight	Intensity and temperature class	ν (Vac)	Term combination	(O−C) λ
4571.971	23	A	15 V*E*, Ti II	21866.297	$a^3H_5-a^3G_4$	
4563.761	16	A	15 V*E*, Ti II	21905.632	$a^3P_1-a^3D_2$	
4559.920	7	B	6 III	21924.083	$b^3F_4-e^3F'_4$	−001
4555.486	30	A	30 II	21945.422	$a^5F_5-b^5F'_4$	
4552.453	30	A	35 II	21960.044	$a^5F_4-b^5F'_3$	
4549.622	10	C	25 V*E*, Ti II	21973.709	$a^3H_6-a^3G_5$	
4548.764	29	A	35 II	21977.853	$a^5F_3-b^5F'_2$	
4544.688	29	A	30 II	21997.564	$a^5F_2-b^5F'_1$	
4533.238	21	B	80 II	22053.109	$a^5F_5-b^5F'_5$	
4527.305	30	A	35 II	22082.026	$a^5F_1-b^5F'_2$	
4522.798	30	A	40 II	22104.030	$a^5F_2-b^5F'_3$	
4518.022	30	A	50 II	22127.394	$a^5F_3-b^5F'_4$	
4512.734	30	A	40 II	22153.325	$a^5F_4-b^5F'_5$	
4503.762	2	D	4*n* IV	22197.454		
4501.270	23	A	25 V*E*, Ti II	22209.745	$a^3G'_4-a^3F'_3$	
4496.146	25	A	20 III	22235.054	$a^5P_3-a^5P'_2$	
4489.089	25	A	20 III	22270.009	$a^5P_2-a^5P'_1$	
4482.688	2	D	10 III	22301.809	$b^3F_4-f^3F'_3$	−003
4481.261	26	A	30 III	22308.910	$a^5P_3-a^5P'_3$	
4474.852	11	A	8 III	22340.862	$b^3F_3-f^3F'_2$	+001
4471.238	25	B	20 III	22358.920	$a^5P_1-a^5P'_2$	
4468.493	25	A	25 V*E*, Ti II	22372.651	$a^3G'_5-a^3F'_4$	
4465.807	25	A	20 III	22386.108	$a^5P_2-a^5P'_3$	
4457.428	29	A	40 II	22428.187	$b^5F_4-f^3F'_4$	−002
4455.321	28	A	30 II	22438.796	$b^5F_3-f^3F'_3$	−001
4453.708	2	D	20 III	22446.921	$a^3G'_3-e^3G_3$	
4453.312	17	C	30 II	22448.916	$b^3F_3-f^3F'_2$	−009
4450.896	29	C	25 III	22461.104	$a^3G'_4-e^3G_4$	
4449.143	30	A	30 III	22469.951	$a^3G'_5-e^3G_5$	
4443.802	21	A	25 V*E*, Ti II	22496.960	$a^3D'_2-a^3F'_3$	
4440.345	20	A	10 III	22514.475	$a^3G'_3-cF'$	
4436.586	5	C	4 III	22533.551	$a^3G'_4-e^3G_5$	
4434.003	14	C	15 III*A*	22546.674	$b^3F_2-f^3F'_3$ and $a^3G'_3-g^3F'_2$	
4430.366	12	C	7 III*A*	22565.183	$b^3F_3-f^3F'_4$	−001
4427.098	30	A	40 III	22581.841	$aG'-bG$	
4426.054	11	C	10 II	22587.166	$a^3G'_4-g^3F'_3$	
4422.823	17	A	10 II	22603.667	$a^3P_2-f^3D_3$	−001
4421.754	9	C	6 III	22609.135	$b^3P_1-f^3D_2$	
4417.274	13	B	15 III	22632.064	$a^3G'_5-g^3F'_4$	
4399.767	6	B	6 V*E*, Ti II	22722.119	$a^3P_2-a^4D_3$	
4395.031	26	A	25 V*E*, Ti II	22746.602	$a^3D'_3-a^3F'_4$	
4393.925	15	B	8 III	22752.326	$bG'-fG$	
4372.383	2	D	3 IV	22864.423		
4369.682	10	C	5*n* IV	22878.552	$aH-gG$	
4360.487	11	B	4 III	22926.798	$a^3D'_3-e^3P'_2$	
4346.104	11	A	5 IV	23002.667	a^3H_4-fG	
4337.916	19	A	10 V*E*, Ti II	23046.089	$a^3D'_3-a^3D_3$	
4325.134	6	A	9*n* III	23114.194	$a^3H^5-f^3G_4$	
4321.655	20	A	8*n* III	23132.801	$a^3H_4-f^3G_3$	
4318.631	25	A	10*n* III	23149.000	$a^3H_6-f^3G_5$	
4314.801	30	A	25 II	23169.542	$a^5F_4-e^3D_3$ and $a^5F_3-e^3D_2$	
4312.861	7	C	7 V*E*, Ti II	23179.966	$a^4P_3-a^4D_3$	
4307.900	21	B	12 V*E*, Ti II	23206.664	$a^4P_2-a^4D_2$	
4305.910	26	A	60 II	23217.386	$a^5F_5-b^5D_4$	
4298.664	29	A	40 II	23256.522	$a^5F_3-b^5D_1$	
4295.751	29	A	22 II	23272.294	$a^5F_1-b^5D_0$	
4294.101	11	C	8 V*E*, Ti II	23281.234	$a^3D'_3-a^3D_3$	
4289.068	27	A	25 II	23308.551	$a^5F_2-b^5D_2$	
4287.405	26	A	22 II	23317.595	$a^5F_4-b^5D_4$	
4286.006	30	A	25 II	23325.204	$a^5F_3-b^5D_3$	
4282.702	23	A	12 III	23343.199	$a^3G'_3-h^3F'_2$	
4281.371	11	C	10 III	23350.459	$a^5F_1-b^5D_2$	
4274.584	13	B	15 III	23387.529	$a^3G'_4-h^3F'_3$ and $a^5F_2-b^5D_3$	

TABLE 1.—*Vacuum arc wave lengths of titanium*—Continued

λ I. A.	Number of observations	Weight	Intensity and temperature class	ν (Vac)	Term combination	(O−C) λ
4263. 134	25	A	15 III	23450. 343	$a^3G'_5-h^3F'_4$	
4258. 523	3	D	4*n* IV	23475. 738	$a^5D_1-b^5D'_2$	
4256. 025	10	B	8*n* III	23489. 513	$a^5D_4-b^5D'_4$	
4249. 114	5	D	5*n* III	23527. 718	$a^5D_3-b^5D'_3$	
4237. 889	10	A	7 III	23590. 035	$bD'-dD$	
4186. 119	25	A	25 III	23881. 766	$aG'-cG$	
4171. 897	8	C	5 V*E*, Ti II	23963. 179	$b^3F_3-c^3D_3$	
4163. 644	8	C	8 V*E*, Ti II	24010. 682	$b^3F_4-c^3D_3$	
4159. 634	11	A	9 III	24033. 828	$a^3D'_3-i^3F'_3$	
4150. 963	8	C	10 III	24084. 030	$a^3D'_3-i^3F'_4$	
4137. 284	10	B	10*n* III	24163. 654	$a^5D_4-b^5P_3$	
4127. 531	12	B	15 III	24220. 752	$a^5G_6-b^5H_6$	
4122. 143	7	C	10 III	24252. 407	$a^5G_5-b^5H_4$	
4112. 708	25	A	20 II	24308. 047	a^3F_4-aG	
4099. 166	8	B	8 III	24388. 346	$a^3D'_3-f^3P'_2$	
4082. 456	24	A	20 III	24488. 173	$a^3P_2-c^3P'_1$	
4078. 471	26	A	30 III	24512. 099	$a^3P_2-c^3P'_2$	
4065. 094	8	B	15 III	24592. 756	$a^3P_1-c^3P'_0$	
4060. 263	23	A	20 III	24622. 015	$a^3P_1-c^3P'_2$	
4058. 139	6	D	7 IV	24634. 904		
4055. 011	22	A	20 III	24653. 908	$a^3P_0-c^3P'_1$	
4035. 828	1	D	10 III	24771. 090	$a^3D'_3-k^3D_3$	
4030. 512	15	A	25*n* III	24803. 759	$a^5F'_5-b^5G'_6$	
4026. 539	10	B	25*n* III	24828. 232	$a^5F'_4-b^5G'_5$	
4024. 573	29	B	35 II	24840. 363	$a^3F_4-b^3F'_3$	000
4017. 771	10	B	15*n* III	24882. 418	$a^5F'_3-b^5G'_3$	
4015. 377	8	B	12*n* III	24897. 249	$a^5F'_1-b^5G'_2$	
4013. 587	8	B	12*n* III	24908. 356	$a^5F'_5-b^5H_6$	
4008. 926	28	A	35 II	24937. 314	$a^3F_3-b^3F'_2$	+001
3998. 635	25	A	100*R* II	25001. 494	$a^3F_4-b^3F'_4$	−003
3989. 758	25	A	80*R* II	25057. 118	$a^3F_3-b^3F'_3$	−002
3981. 761	26	A	70*R* II	25107. 441	$a^3F_3-b^3F'_2$	+001
3964. 269	23	B	35 II	25218. 220	$a^3F_3-b^3F'_4$	−001
3962. 851	23	A	35 II	25227. 247	$a^3F_2-b^3F'_3$	−001
3958. 206	25	B	80 II	25256. 850	$a^3F_4-b^3D_3$	+001
3956. 336	28	A	60 II	25268. 790	$a^3F_3-b^3D_2$	+002
3948. 670	26	B	60 II	25317. 847	$a^3F_2-b^3D_1$	+004
3947. 770	25	B	40 II	25323. 617	$a^3F_3-a^3P'_2$	
3929. 875	25	B	40 II	25438. 923	$a^3F_3-b^3D_3$	+001
3924. 527	28	A	50 II	25473. 592	$a^3F_3-b^3D_3$	000
3921. 423	16	B	30 II	25493. 757	$a^3F_2-a^3P'_2$	
3914. 334	20	B	35 II	25539. 920	$a^3F_4-c^3F'_4$	
3913. 464	11	B	40 V*E*, Ti II	25545. 603	$a^3G'_4-a^3G_4$	
3904. 785	26	A	40*n* II	25602. 379	$aD'-bF'$	
3900. 546	7	D	50 V*E*, Ti II	25630. 202	$a^3G'_5-a^3G_5$	
3895. 243	6	C	30*n* III	25665. 092	$a^5G_6-b^5H_6$	
3875. 262	14	C	20*n* III	25797. 424	$a^3F_2-c^3F_3$ and $a^5G_4-b^5G'_5$	
3856. 446	2	D	15*n* IV	25856. 242	$a^5G_6-b^5H_6$	
3798. 276	3	D	6 IV	26320. 291	$b^3F_2-g^3D_1$	
3786. 043	23	C	20 II	26405. 331	$aD'-aP'$	
3771. 652	24	A	25 I	26506. 075	$a^3F_4-d^3F'_3$	000
3761. 320	24	B	40 IV *Er*, Ti II	26578. 885	$a^3F_3-a^3F'_3$	
3759. 291	23	B	40 IV *Er*, Ti II	26593. 234	$a^3F_4-a^3F'_4$	
3752. 860	24	B	80*r* I	26638. 799	$a^3F_4-d^3F'_4$	−001
3741. 059	25	B	60*r* I	26722. 827	$a^3F_3-d^3F'_3$	−002
3729. 806	25	A	50*r* I	26803. 450	$a^3F_2-d^3F'_2$	+001
3725. 155	5	C	20 III	26836. 920	$a^3P_2-b^3S_1$	
3724. 570	7	C	20 III	26841. 134	$aG'-dG$	
3722. 568	14	B	15 II	26855. 565	$a^3F_3-d^3F'_4$	−004
3717. 393	14	A	20 I	26892. 955	$a^3F_2-d^3F'_3$	−001
3694. 445	9	C	10 III	27059. 989	$b^3F_3-h^3D_3$	
3689. 916	14	A	15 I	27093. 208	$a^3F_3-c^3D_3$	+001
3685. 192	17	B	40 IV *Er*, Ti II	27127. 936		
3671. 672	14	A	20 I	27227. 821	$a^3F_4-b^3G_4$	000

TABLE 1.—*Vacuum arc wave lengths of titanium*—Continued

λ I. A.	Number of observations	Weight	Intensity and temperature class	ν (Vac)	Term combination	(O−C) λ
3668.965	14	B	15 I	27247.912	$a^3F_3-c^3D_2$	−001
3660.631	12	A	12 I	27309.943	$a^3F_2-c^3D_3$	000
3658.097	12	B	20 I	27328.863	$a^3F_3-b^3G_3$	+005
3654.592	10	B	15 I	27355.073	$a^3F_2-c^3D_1$	−001
3653.497	15	C	100r I	27363.270	$a^3F_4-b^3G_5$	+002
3646.198	9	A	12 I	27418.045	$a^3F_2-c^3D_2$	−001
3642.675	14	B	80r I	27444.563	$a^3F_3-b^3G_4$	000
3641.330	6	B	10 V *E*, Ti II	27454.697	$a^3P_2-a^3S_1$	
3635.462	12	B	80r I	27499.014	$a^3F_2-b^3G_3$	+003
3624.826	10	B	8 V *E*, Ti II	27579.694	$a^2P_1-a^2S_1$	
3610.154	9	B	12 III	27691.779	$a\ D'-b\ P'$	
3598.714	12	A	15 III	27779.807	$a\ D'-c\ D$	
3596.048	9	B	10 V *E*, Ti II	27800.404	$a^3F_4-a^4D_3$	
3547.029	5	B	15 IV	28184.583	$a\ G'-d\ F'$	
3535.408	9	A	10 V *E*, Ti II	28277.224	$b^3P_2-c^3D_3$	
3510.840	12	B	10 V *Er*, Ti II	28475.101	$b^4G'_4-b^3G_4$	
3504.890	12	A	8 V *Er*, Ti II	28523.436	$b^4G'_5-b^3G_5$	
3491.053	3	D	8 III *Eru*, Ti II	28636.491	$b^4F_3-a^4G_3$	
3480.525	5	D	12 II	28723.103	$a^3P_2-d^3P'_2$	
3477.181	9	C	15 III *Eru*, Ti II	28750.726	$b^4F_3-a^4G_4$	
3461.496	12	A	20 III *Eru*, Ti II	28881.000	$b^4F_4-a^4G_5$	
3444.306	12	C	15 III *Eru*, Ti II	29025.141	$b^4F_5-a^4G_6$	
3394.574	12	B	15 III *Eru*, Ti II	29450.353	$a^4F_3-a^4G_3$	
3387.834	12	B	15 III *Eru*, Ti II	29508.944	$a^4F_4-a^4G_4$	
3385.944	12	B	40r II	29525.411	$a^3F_4-e^3D_3$	000
3383.761	10	A	40 III *Eru*, Ti II	29544.463	$a^4F_2-a^4G_3$	
3380.278	12	A	15 III *Eru*, Ti II	29574.905	$a^4F_3-a^4G_5$	
3377.577	9	C	30r I	29598.557	$a^3F_3-e^3D_2$	+001
3371.447	4	D	80*R* II	29652.367	$a^3F_4-c^3G_5$	+001
3370.436	6	C	40r II	29661.260	$a^3F_2-e^3D_1$	+001
3361.213	11	B	40 III *Er*, Ti II	29742.652	$a^4F_4-a^4G_5$	
3358.271	5	C	10 I	29768.709	$a^3F_3-e^3D_2$	−002
3354.634	11	B	60r II	29800.975	$a^3F_3-c^3G_4$	000
3349.399	11	C	40 II *Er*, Ti II	29847.557	$a^4F_5-a^4G_6$	
3341.875	11	B	50r II	29914.755	$a^3F_2-c^3G_3$	+003
3340.344	10	C	15 III *Eru*, Ti II	29928.462	$b^4F_2-a^4F'_3$	
3335.192	12	B	20 III *Eru*, Ti II	29974.689	$b^4F_3-a^4F'_3$	
3332.111	8	B	8 V *Er*, Ti II	30002.406	$b^4P_3-a^4S_2$	
3329.455	9	B	20 III *Eru*, Ti II	30026.342	$b^4F_4-a^4F'_4$	
3326.762	2	D	5 III *Eru*, Ti II	30050.641	$b^4F_2-a^4F'_3$	
3322.936	11	A	20 III *Eru*, Ti II	30085.241	$b^4F_3-a^4F'_3$	
3318.024	7	A	8 III *Eru*, Ti II	30129.784	$b^4F_3-a^4F'_4$	
3314.422	10	B	10 I	30162.528	$a^3P_2-h^3D_3$	
3292.078	10	B	20 I	30367.234	$aD'-cF'$	
3287.657	10	B	10 V *Er*, Ti II	30408.067	$b^3G'_4-a^3H'_5$	
3261.596	8	B	25 V *Er*, Ti II	30651.031	$b^3G'_5-a^3H'_6$ $b^4P_2-b^4D_2$	
3241.984	10	A	40 III *Er*, Ti II	30836.445	$a^4F_2-a^4F'_2$	
3239.037	10	C	40 III *Er*, Ti II	30864.588	$a^4F_3-a^4F'_3$	
3236.573	10	B	50 III *Er*, Ti II	30888.089	$a^4F_4-a^4F'_4$	
3234.517	10	B	60 III *Er*, Ti II	30907.726	$a^4F_5-a^4F'_5$	
3229.397	4	D	10 V *Eru*, Ti II	30956.628	$a^2G'_4-b^2F'_4$	
3222.843	9	A	15 III *Er*, Ti II	31019.583	$a^4F_3-a^4F'_4$	
3217.056	9	A	15 III *Er*, Ti II	31075.376	$a^4F_4-a^4F'_5$	
3214.240	8	C	12 I	31102.603	$a^3F_4-d^3G_4$	+002
3202.535	9	A	12 V *Er*, Ti II	31216.276	$a^2D'_3-b^2F'_3$	
3199.915	10	B	100*R* II	31241.828	$a^3F_4-d^3G_5$	000
3191.994	9	A	80*R* II	31319.353	$a^3F_3-d^3G_4$	000
3190.801	4	D	20 IV *Er*, Ti II	31331.070	$a^2D'_3-b^2F'_4$	
3186.451	10	A	60r II	31373.839	$a^3F_2-d^3G_3$	+002
3168.519	10	A	30 III *Eru*, Ti II	31551.385	$b^4F_3-a^4D_4$	
3161.755	6	D	20 III *Eru*, Ti II	31618.884	$b^4F_2-a^4D_2$	
3148.033	2	D	12 IV *E*, Ti II	31756.698	$a^4F_2-a^2D_2$	
3130.804	3	D	15 IV, Ti II	31931.457	$a^4F_3-a^2D_3$	
3088.027	10	A	60 III *Er*, Ti II	32373.764	$a^4F_5-a^4D_4$	
3078.645	10	A	45 III *Er*, Ti II	32472.424	$a^4F_4-a^4D_3$	
3075.225	10	C	40 III *Er*, Ti II	32508.527	$a^4F_3-a^4D_2$	
2956.133	7	C	70*R* II	33818.127	$a^3F_4-f^3F'_4$	000
2948.255	8	A	60r II	33908.489	$a^3F_3-f^3F'_3$	000
2941.905	7	C	60r II	33980.630	$a^3F_3-f^3F'_3$	+004

2. COMPARISON WITH OTHER OBSERVATIONS

Two other observers have measured wave lengths in the vacuum arc spectrum of titanium. In 1922 Brown [13] published a list of more than 100 wave lengths between 4263 and 6261 A determined by interference methods in terms of the primary standard—the red ray of cadmium. This was followed two years later by a more extensive list by Crew,[14] who observed the region from 3653 to 6366 A with a plane grating giving high dispersion. There is most excellent agreement between the Bureau of Standards wave lengths and those of Brown in the interval from 4262 to 5200 A. Most of the differences, Bureau of Standards *minus* Brown, are less than 0.003 A and exhibit no systematic shift between the two sets of results, the mean of the differences being +0.0001 A. Between 5200 and 5800 A Brown's list contains 13 Ti lines, of which 11 may be compared with the Bureau of Standards determinations. Of these, there are two positive differences, three zeros, and six negative differences, the mean value of Bureau of Standards *minus* Brown being −0.001 A. From 5800 to the end of Brown's list, his wave lengths are systematically longer than the Bureau of Standards values, the difference increasing from −0.001 A at 5800 A to −0.004 A at 5260 A.

The comparison of the Bureau of Standards wave lengths with Crew's is limited to the region 3653 to 4263 A, his wave lengths longer than 4263 A being based on those of Brown described above. The differences, Bureau of Standards *minus* Crew, change linearly from −0.005 A at 3653 to +0.002 A at 3800 A, being zero at 3750 A. From 3800 to 4000 A the difference is practically constant, amounting to +0.002 A. At 4000 A there is an abrupt increase in the difference to +0.010 A from which it decreases linearly to −0.010 A at 4263 A, being zero in the vicinity of 4130 A.

3. COMPUTATION OF WAVE LENGTHS FROM SPECTRAL TERMS

Classification of the lines of a spectrum as the difference of two spectral terms permits a calculation of the wave lengths of the lines if the term values are known. In recent years rapid progress has been made in the extension of our knowledge of the structure of spectra not only of neutral atoms which emit arc spectra, but also of ionized atoms which emit the various stages or orders of spark spectra. Such analyses of the spectrum of titanium have been made by Kiess and Kiess [15] and by Russell.[16] From the work of these

[13] Astrophys. J., **56**, p. 53; 1922.
[14] Astrophys. J., **60**, p. 108; 1924.
[15] J. Opt. Soc. Am. and Rev. Sci. Inst., **8**, p. 607; 1924.
[16] Astrophys. J. **66**, pp. 283 and 347; 1927.

investigators have been taken the term combinations or series classifications of the lines given in column 6 of Table 1. The numerical values of the term combinations are the wave numbers in vacuum of the lines as entered in column 5.

If the terms involved in the production of the spectrum can be determined solely from lines measured in the yellow and red—that is, in the vicinity of the neon standards—then it is possible to calculate from them the wave lengths of lines in the blue and violet and thereby check the accuracy of observations remote from the standards. Such an ideal procedure, however, is not entirely possible in the case of titanium owing to the low intensities and consequent paucity of the longer Ti lines in the vacuum arc. An alternative procedure for testing the scale of a wave-length interval by means of cyclical term combinations, such as carried out by Meggers [17] for the iron spectrum, was likewise not feasible for Ti because of the small number of cycles which could be formed from the wave lengths of Table 1. It was, therefore, decided to set up a system of terms based not only on the longer wave lengths of the table, but also on the relative term separations as given by observations throughout the measured wave-length interval. The degree of the constancy of these term separations is exhibited in Table 2, wherein are collected various differences used in calculating the relative values of the low terms.

TABLE 2.—*Constancy of term differences throughout the spectrum*

$a^3F_4-a^3F_3$	$a^3F_3-a^3F_2$	$a^3F_4-b^3F_4$	$a^3F_3-b^3F_3$	$a^3F_2-b^3F_2$	$a^3F_4-a^3P_2$	$a^3F_3-a^3P_1$	$a^3F_2-a^3P_0$
216.722	170.122	11389.934	11469.688	11531.789	8215.486	8322.307	8436.646
.726	.129	.960	.672	.786	.488	.310	.597
.755	.129	.955	.686	.800	.467		
.752	.127	.952	.701				
.744	.106	.940	.693				
.742	.133	.947	.688				
.741	.150	.940					
.749	.133						
.735	.151						
	.140						
216.741	170.132	11389.947	11469.688	11531.792	8215.480	8322.308	8436.622

The mean values of the term differences of Table 2 were used in deriving the values of the terms a^3F, b^3F, and a^3P of Table 3. From these the remainder of Table 3 was calculated by the joint use of wave numbers shorter than 21,300.000 from Table 1 and relative term separations similar to those of Table 2. Although many of the well-observed lines of Table 1 belong to the singlet and quintet systems of Ti I, yet it was not possible to derive good term values for these systems by adhering to the limitations set for the derivation of the triplet system terms. The wave numbers calculated from

[17] Astrophys. J., **60**, p. 60 1924.

these terms were converted into wave lengths which were compared with the observed values of Table 1. The results of the comparison are shown in the last column of Table 1, where the residuals O−C are entered. The algebraic sum of the differences O−C for the interval 4700–2941 A is practically zero, although negative residuals predominate in the region 4700–3700 A, and positive residuals in the region 3700–2941 A. However, since the wave lengths would require, in each of these regions, a mean correction of less than 0.001 A to reduce the sums of the residuals to zero, the representation of the wave lengths by means of the terms of Table 3 is regarded as satisfactory and is interpreted as indicating that the blue and violet lines have been measured to the same scale as those longer than 4700 A. For lines longer than 4700 A the majority of the residuals are necessarily zero, since the lines were used directly in the computation of the terms. With one exception the residuals greater than 0.002 A in this region refer to lines observed only a few times.

TABLE 3.—*Terms in the triplet system of titanium*

a^3F_4	386.873	a^3D_3	20126.072	$a^3F'_4$	19573.980	a^3G_5	21739.743	$a^3H'_6$	32013.555
	216.741		*120.023*		*152.400*		*151.223*		*99.251*
a^3F_3	170.132	a^3D_2	20006.049	$a^3F'_3$	19421.580	a^3G^4	21588.520	$a^3H'_5$	31914.304
	170.132		*68.171*		*98.577*		*118.986*		*84.288*
a^3F_2	0.000	a^3D_1	19937.878	$a^3F'_2$	19323.003	a^3G_3	21469.534	$a^3H'_3$	31830.016
b^3F_4	11776.820	b^3D_3	25643.724	$b^3F'_4$	25388.345	b^3G_5	27750.156	$b^3H'_6$	35685.188
	137.000		*204.794*		*161.109*		*135.463*		*125.526*
b^3F_3	11639.820	b^3D_2	25438.930	$b^3F'_3$	25227.236	b^3G_4	27614.693	$b^3H'_5$	35559.662
	108.008		*121.088*		*119.783*		*115.660*		*105.563*
b^3F_2	11531.812	b^3D_1	25317.842	$b^3F'_2$	25107.453	b^3G_3	27499.033	$b^3H'_4$	35454.099
a^3P_2	8602.353	c^3D_3	27480.077	$d^3F'_4$	27025.667	c^3G_5	30039.246		
	109.916		*62.040*		*152.721*		*68.140*		
a^3P_1	8492.437	c^3D_2	27418.037	$d^3F'_3$	26892.946	c^3G_4	29971.106		
	55.807		*62.972*		*89.484*		*56.333*		
a^3P_0	8436.630	c^3D_1	27355.065	$d^3F'_2$	26803.462	c^3G_3	29914.773		
$a^3G'_5$	15220.400	e^3D_3	29912.292	e^3F_4	33700.897	d^3G_5	31628.698		
	63.597		*143.606*		*20.735*		*159.212*		
$a^3G'_4$	15156.803	e^3D_2	29768.686	$e^3F'_3$	33680.162	d^3G_4	31489.486		
	48.650		*107.414*		*24.264*		*115.624*		
$a^3G'_3$	15108.153	e^3D_1	29661.272	$e^3F'_2$	33655.898	d^3G_3	31373.862		
a^3H_6	18192.594	f^3D_3	31206.014	f^3F_4	34205.001				
	51.342		*15.351*		*126.389*				
a^3H_5	18141.252	f^3D_2	31190.663	$f^3F'_3$	34078.612				
			6.574		*97.927*				
a^3H_4		f^3D_1	31184.089	$f^3F'_2$	33980.685				

IV. RESULTS FOR OTHER ELEMENTS

In Tables 4, 5, and 6 which follow are given the vacuum arc wave lengths of a few lines of elements which appeared as impurities in the titanium or were especially observed to supply additional data for the solar work. The most abundant impurity in the titanium was iron; in lesser amounts were calcium, aluminum, chromium, vanadium, and sodium. The elements especially observed for wave lengths in the yellow and red were calcium, barium, manganese, and nickel, the observations being made at the same time as the first series of titanium. Owing to the fact that a copper rod was used

nearly always for the negative electrode, 26 lines of this element were also measured on the spectrograms of all three series and are given below.

TABLE 4.—*Vacuum arc wave lengths of iron*

λI.A	Number of observations	Weight	Intensity, temperature, and pressure classes	Bureau of Standards *minus* Babcock	λI.A	Number of observations	Weight	Intensity, temperature, and pressure classes	Bureau of Standards *minus* Babcock
5371.488	5	D	50 I*B* *a*	−005	3799.554	4	C	50 II	+005
5328.044	10	A	50 I*B* *a*	+002	3795.005	6	C	60 II *b*	+001
5269.539	13	A	60 I*B* *a*	−002	3767.193	14	A	80*r* II *b*	000
4415.123	6	A	20 II *b*	−002	3763.791	14	A	100*r* II *b*	000
4383.545	25	A	45*r* II *b*	−003	3758.237	7	C	150*R* II *b*	+003
					3749.488	8	C	200*R* II *b*	+001
4271.762	22	A	35 II *b*	−002					
4260.476	12	B	35 III *d*	−004	3748.264	8	B	60*R* I*A* *a*	000
4250.789	9	A	25 II *b*	−001	3745.560	14	A	100*R* I	
4235.937	6	D	25 II *d*	−005	3737.132	13	B	150*R* I *a*	−002
4202.030	10	A	30 II *b*	−002	3734.865	17	B	300*R* II	
					3733.320	11	B	40*r* I*A* *a*	+002
4143.869	7	B	15 III *b*	−002	3727.621	10	B	50*r* II *b*	000
4132.060	11	B	25 II *b*	−001					
4071.740	22	A	40 II *b*	−001	3719.934	13	B	250*R* I *a*	−003
4045.813	27	A	60*r* II *b*	−001	3709.256	8	C	75*r* II *b*	+008
4005.244	4	C	25 II *b*	000	3705.566	13	A	100*r* I *a*	−001
					3687.454	12	B	40*r* I *b*	−005
3930.294	2	C	25*R* I*B* *a*	−004	3679.915	14	A	40*r* I*A* *a*	000
3927.919	14	A	30*R* I*B* *a*	−002					
3922.914	5	C	25*R* I*B* *a*	+001	3647.844	14	A	100*R* I *b*	+001
3920.261	5	D	20*r* I*B* *a*	+002	3631.465	14	A	125*R* I *b*	000
3899.712	3	D	30*R* I*B* *a*	+004	3618.769	14	A	125*R* I *b*	000
					3608.861	8	B	100*r* I	−001
3886.281	24	B	40*R* I*B* *a*	−003					
3859.905	8	C	300*R* I		3581.194	12	A	250*R* I	−002
3856.377	2	C	50*r* I*A*	+004	3570.099	11	B	100*R* I	
3834.221	12	A	100*r* II *b*	−003	3565.380	12	B	60*r* II	
3827.821	2	C	75*r* II *b*	−003	3558.517	11	B	30 II	−001
3825.881	4	B	200*R* II *b*	−003	3497.844	4	C	40 I	+001
3824.447	3	C	50*r* I*A*	+002	3465.862	11	B	60*r* I	000
3820.428	20	A	250*R* II	000	3440.990	12	C	75*R* I	
3815.844	21	A	100*r* II *b*	+002	3020.635	6	D	200*R* I	
3806.711	2	D	10 III	+013					

TABLE 5.—*Vacuum arc wave lengths of copper*

λ I. A.	Number of observations	Weight	Intensities	Bureau of Standards *minus* Wolfsohn		λ I. A.	Number of observations	Weight	Intensities	Bureau of Standards *minus* Wolfsohn	
				Vacuum	Air					Vacuum	Air
5782.132*	31	A	8*r*	−004		3530.382	9	B	7		
5700.239*	23	A	8*r*			3337.845	10	A	8		
5292.519	9	C	6			3279.815	10	B	5	−017	−005
5220.070*	13	A	6	−040	−008	3273.956*	7	A	10*R*	−018	−005
5218.202	27	A	10	−031	000						
						3247.540*	8	B	10*R*	−016	−002
5153.237*	27	A	8	−035	+004	3208.230	8	B	6	−020	−010
5105.542	23	A	7	−017	−009	3194.096	8	B	8	−018	
4704.593	6	D	4			3063.411	10	A	7	−015	−008
4651.124	14	B	8	−025							
4530.786*	11	A	6	−009		3036.101	10	B	8	−013	−006
						3010.838	10	A	7	−013	−007
4509.374	10	B	6	−015	−013	2961.164	4	D	9	−015	−009
4480.360*	6	C	7	−004		2824.369	4	B	10	−013	
4062.639	8	C	10								
4022.627	11	A	10								

TABLE 6.—*Vacuum arc wave lengths of Na, Al, Ca, V, Cr, Mn, Ni, and Ba*

λ I. A.	Number of observations	Weight	Intensity	Temperature class	λ I. A.	Number of observations	Weight	Intensity	Temperature class
SODIUM					MANGANESE				
5895. 927	5	A	8*R*		6021. 798	12	A	50	III
5889. 954	8	A	10*R*		6016. 639	9	A	40	III
					6013. 490	4	B	30	III
ALUMINUM					NICKEL				
3961. 527	6	B	10*R*						
3944. 009	6	B	10*R*		6767. 778	10	A	20	I
					6643. 641	10	A	20	I
CALCIUM					6314. 666	10	A	15	II
					6256. 365	10	A	15	I
6499. 651	3	C	30	II					
6493. 780	8	A	80	II	6176. 813	6	A	12	V
6471. 661	4	B	40	II	6108. 121	6	A	8	II
6462. 565	7	A	125	II	5892. 878	6	A	12	II
6449. 809	7	A	50	II					
					BARIUM				
6439. 073	7	A	150	II					
6169. 554	3	B	40	III	6595. 328	4	A	200	I
6169. 048	4	C	25	III	6527. 314	5	A	250	I
6162. 173	7	A	150	II	6498. 762	6	A	300*r*	II
6122. 217	8	A	100	II	6496. 90?	6	A	600*r*	III
					6482. 912	3	B	200	II
6102. 720	7	A	80	II					
5857. 451	6	A	100	III	6450. 854	3	A	125	I
4226. 728	3	C	500*R*	I	6341. 683	3	A	150	I
3968. 469	12	A	350*R*	II	6141. 716	5	A	600*r*	III
3933. 669	4	C	400*R*	II	6110. 785	5	A	300*r*	II
					6063. 118	3	A	200	II
VANADIUM									
					6019. 474	2	C	100	II
4379. 234	7	B	150*r*	II	5997. 091	3	A	100	II
					5971 701	3	A	100	II
CHROMIUM					5853. 679	4	A	200	III
4254. 337	19	A	500*R*	II					
3593. 488	12	B	160*R*	II					
3578. 687	11	B	200*R*	II					

1. IRON

The iron lines whose wave lengths are given in the first column of Table 4 all originate in the lowest or the low metastable states of the iron atom. They are, accordingly, easily excited and appear with great intensity. In arcs in air most of them are reversed. The character of the lines in arcs in air and their behavior in the vacuum furnace are described in columns 4 and 5, the data for which are taken from King.[18] In the vacuum arc, however, these lines become narrow and give sharp interference fringes with high orders, a phenomenon pointed out long ago by Fabry and Buisson.[19] With two exceptions these lines belong to pressure classes *a* and *b* which means that they experience the least displacement with increasing pressure. We should, therefore, expect to find very little difference between their wave lengths in vacuum and in air, the amount of the displacement increasing with wave length. Such, indeed, is the case. Quite

[18] Astrophys. J., **37**, p. 239; 1913; **56**, p. 318; 1922.
[19] J. de Physique (IV), **9**, p. 947; 1910.

recently Babcock [20] has published interferometer measurements of iron wave lengths emitted by arcs in air. The comparison of the Bureau of Standards values with his is shown in the last column of Table 4. In the ultra-violet—that is, the region of wave lengths shorter than 3922 A—the residuals, Bureau of Standards *minus* Babcock, are about equally distributed among positive and negative values, being in the mean +0.0007 A. But for all lines longer than 3922 A the residuals, Bureau of Standards *minus* Babcock, are negative, with one exception, the mean being −0.002 A.

2. COPPER

The copper lines which were measured are listed in Table 5. Of these, the pair at 5700 and 5782 A in the yellow, and the *raies ultimes*, 3247 and 3274 A, always appeared reversed. The intensities assigned to the lines are taken from Kayser's *Tabelle der Hauptlinien*. Four pairs of lines in this table, marked with an asterisk (*), involve the term $^2P_{1,2}$ as may be seen by reference to Shenstone's [21] classification of the Cu arc spectrum. They may, therefore, be used to determine the separation of the components of this term, and thereby check the relative accuracy of the measurements. The four values of $^2P_2 - {}^2P_1$ are: 248.392, 248.377, 248.335, and 248.364. The low value of the third is accounted for by the fact that the wave length 4480.360 A which enters into its determination is affected by the Ti line at 4480.60. A correction of −0.009 A applied to the tabulated wave length would give a value of $^2P_2 - {}^2P_1$ equal to the mean of the other three determinations.

The vacuum arc spectrum of Cu has been measured recently by Wolfsohn [22] who photographed it in juxtaposition with the spectrum of the arc in air, using the high dispersion afforded by the grating spectrograph at Bonn. His vacuum values are systematically larger than his air values which he interprets as a pressure shift toward the violet for lines emitted by the arc in air. A comparison of the Bureau of Standards wave lengths with Wolfsohn's is given in the last two columns of Table 5, which shows that his conclusions concerning the pressure shift toward the violet are not verified. In fact, assuming the correctness of his arc-in-air measurements the residuals, Bureau of Standards *minus* Wolfsohn, indicate for copper the same type of pressure shift as has been found for all other spectra which have been investigated.

[20] Astrophys. J. **66**, p. 256; 1927.
[21] Phys. Rev., **28**, p. 449; 1926.
[22] Annalen der Physik (IV), **80**, p. 415; 1926.

3. Na, Al, Ca, V, Cr, Mn, Ni, Ba

In Table 6 are listed some wave lengths of Na, Al, Ca, V, Cr, Mn, Ni, and Ba. Some of these elements, as stated above, occurred as impurities in the electrodes. Ca, Mn, Ni, and Ba were especially investigated to furnish additional standards in the red for comparison with the solar wave lengths. The intensities and temperature classes given for each line are those assigned by King, except for Na, and Al, for which the estimates given by Kayser [23] are quoted. The impurity lines are in all cases either the *raies ultimes* or persistent lines of the corresponding elements, and all appear among the Fraunhofer lines of the sun's spectrum.

V. ACKNOWLEDGMENTS

The work described in the foregoing pages has been in progress at the Bureau of Standards for several years. Various persons have cooperated with me in carrying it to completion, and it is a pleasure to acknowledge here my appreciation of their assistance. D. D. Laun, formerly of the bureau staff, did a large share of the observing and computations required for the work with the silver-on-glass interferometers. Dr. K. Burns, of the Allegheny Observatory, shared in the observing with the platinum-on-quartz interferometers; and B. W. Scribner, jr., of the bureau staff, has assisted in the reductions of the last series of observations. Finally, to Prof. H. N. Russell, of Princeton University, I owe my thanks for placing at my disposal his unpublished results on the classification of the titanium arc and spark spectra.

WASHINGTON, December 19, 1927.

[23] Kayser, Tabelle der Hauptlinien. Julius Springer, Berlin, 1926.

ANALYSIS OF BAUXITE AND OF REFRACTORIES OF HIGH ALUMINA CONTENT

By G. E. F. Lundell and J. I. Hoffman

ABSTRACT

A study has been made of the analytical details involved in the analysis of bauxite and burnt refractories of high alumina content. The work has shown that an accurate analysis of these materials is a far more difficult problem than it is ordinarily thought to be. In spite of the fact that the determination of alumina is usually regarded as very simple, extreme values of 54.84 and 56.68 per cent were reported by the analysts who cooperated on the analysis of the Bureau of Standards standard sample of bauxite No. 69 (actual Al_2O_3, 55.06 per cent). The results for alumina and silica reported in the analysis of the standard burnt refractories Nos. 76, 77, and 78 were even less satisfactory. The improper drying of bauxite and the difficulty of putting burnt refractories into complete solution were found to be sources of error.

Other sources of error, such as improper ignition of precipitates of aluminum hydroxide, misleading corrections for impurities derived from reagents, etc., are pointed out. An umpire method is given for the determination of SiO_2, Al_2O_3, P_2O_5, Cr_2O_3, V_2O_5, Fe_2O_3, TiO_2, ZrO_2, CaO, and MgO. In addition, a routine method for Al_2O_3 is described. In this method the solution of the sample is divided into three aliquots. In the first aliquot the Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, and V_2O_5 are precipitated by NH_4OH. In the second aliquot the Fe_2O_3, TiO_2, ZrO_2, and V_2O_5 are precipitated by cupferron. In the third aliquot the P_2O_5 is determined. The Al_2O_3 is then found by difference.

CONTENTS

	Page
I. General considerations	92
II. Methods of analysis	93
1. Precautions	93
(*a*) Drying	93
(*b*) Solution of the sample	93
(*c*) Silica	94
(*d*) Alumina	95
2. Umpire method for the analysis of bauxite or refractories of high alumina content	96
(*a*) Drying	96
(*b*) Solution of the sample	97
(*c*) Determination of silica	97
(*d*) Determination of the mixed oxides	98
(*e*) Recovery of silica	98
(*f*) Determination of P_2O_5, Cr_2O_3, and V_2O_5	99

II. Methods of analysis—Continued.
2. Umpire method for the analysis of bauxite or refractories of high alumina content—Continued Page
(*g*) Determination of Fe_2O_3, TiO_2, and ZrO_2 (HfO_2) 100
(*h*) Determination of lime and magnesia 101
(*i*) Determination of the alkalies 102
3. Routine method for the determination of alumina in bauxite or refractories of high alumina content 102
(*a*) Precipitation by ammonium hydroxide 103
(*b*) Precipitation of Fe_2O_3, TiO_2, etc., by cupferron 103
(*c*) Determination of P_2O_5 103

I. GENERAL CONSIDERATIONS

An accurate analysis of bauxite or of refractories of high alumina content is a far more difficult problem than is ordinarily thought. For example, in the A. S. T. M. Standards (1924), page 749, it is stated that—

> It shall be considered satisfactory if the differences between check determinations (in refractories) do not exceed the following limits: For silica or other constituents amounting to 30 per cent or over, 0.3 per cent; for alumina or other constituents amounting to 10 to 30 per cent, 0.2 per cent; and for any other constituent amounting to under 10 per cent, 0.1 per cent.

In contrast to these expectations the data given in Table 1 show the extreme values and the average deviation from the standard values for the first analyses reported on Bureau of Standards standard samples of burnt refractories Nos. 76, 77, and 78. Furthermore, in determinations of the percentage of Al_2O_3 in the bureau sample of bauxite No. 69 (55.06 per cent Al_2O_3) the extreme values reported were 54.84 and 56.68, and the average deviation from the standard value was 0.59 per cent.

TABLE 1.—*Results reported in first analyses of Bureau of Standards analyzed refractories*

Constituent	Sample No. 76			Sample No. 77			Sample No. 78		
	Recommended value	Extreme values	Average deviation	Recommended value	Extreme values	Average deviation	Recommended value	Extreme values	Average deviation
SiO_2	54.68	53.02–55.00	0.43	32.38	30.20–32.76	0.58	20.69	18.26–21.64	0.51
Al_2O_3	37.67	37.47–40.81	.76	59.39	58.82–61.67	1.33	69.97	69.23–74.36	1.68
Fe_2O_3	2.38	.85– 3.69	.37	.90	.75– 3.46	.46	.79	.63– 3.38	.43
TiO_2	2.21	.10– 2.70	.35	2.93	.14– 3.10	.35	3.37	.17– 3.60	.59
CaO	.27	.11– .95	.21	.26	.19– .48	.10	.38	.28– .65	.09
MgO	.58	.08– .71	.23	.50	.09– .58	.18	.51	.03– .70	.19
K_2O	1.37	.87– 1.43	.26	2.11	1.16– 2.10	.63	2.83	1.84– 2.90	.66
Na_2O	.38	.09– 1.66	.53	.86	.43– 2.17	.59	.53	.32– 1.72	.47

It is significant that the differences between the determinations for SiO_2 and for Al_2O_3 were from 7 to 17 times greater than the specified tolerances, and that out of 28 analyses of the refractories 17 results for SiO_2 were lower and 11 were higher than the actual content, while for Al_2O_3, 6 results were lower and 22 were higher.

It is apparent that there is room for considerable improvement in the analysis of such materials, in spite of the attention that has been paid to methods for determining SiO_2, Al_2O_3, and the like. This paper accordingly sets forth suggested umpire procedures, together with such precautions as have been found necessary. In addition, a routine method is suggested for the determination of Al_2O_3, particularly in bauxite, which provides a simple direct determination of P_2O_5 and obviates the necessity of separate determinations of and deduction for such constituents as Fe_2O_3, TiO_2, ZrO_2, and V_2O_5, all of which may be present and must be guarded against.

II. METHODS OF ANALYSIS

1. PRECAUTIONS

(*a*) DRYING.—The moisture content of powdered bauxite varies with atmospheric conditions. In tests made at the Bureau of Standards it was found necessary to dry samples for two hours at 140° C. in order to obtain reproducible results. Material thus dried is so hygroscopic that each portion of sample taken for analysis must be separately dried. Burnt refractories present very little difficulty in drying. Reproducible samples can be obtained by drying for one hour at 105 to 110° C., and the dried samples are not appreciably hygroscopic.

(*b*) SOLUTION OF THE SAMPLE.—Bauxite can be almost entirely decomposed by a mixture of HF, HNO_3, and H_2SO_4. Such an attack is more convenient than a fusion procedure because the introduction of foreign salts is avoided and SiO_2 is eliminated. HF must afterwards be entirely expelled by fuming with H_2SO_4, or the subsequent precipitation of aluminum by NH_4OH will be incomplete, and any insoluble residue must be recovered, fused, and put into solution.

Burnt refractories do not respond as well to a wet attack. For these, as well as for bauxite, when SiO_2 is to be determined, recourse must be had to a fusion method. Na_2CO_3, Na_2O_2, $K_2S_2O_7$, or $Na_2S_2O_7$ are satisfactory fluxes. At the Bureau of Standards 7 to 10 g of Na_2CO_3 was used for the fusion of a 1 g sample, and the full temperature of a Méker burner was maintained for at least one hour. Of the cooperating analysts, W. F. Muehlberg, of the Newburgh Steel Works, obtained satisfactory results in the analysis of bauxite by exploding the sample in a mixture of Na_2O_2 and sugar carbon,[1] while L. P. Chase,[2] of the Illinois Steel Co., fused the burnt refractories with $K_2S_2O_7$. According to M. O. Lamar,[2] of the Norton Co.,

[1] W. F. Muehlberg, Ind. Eng. Chem., **17**, p. 690; 1925.
[2] Private communication.

satisfactory fusions of calcined bauxite are obtained through the use of equal parts of Na_2CO_3 and fused $Na_2B_4O_7$.[3]

The melt can be dissolved in dilute HCl or H_2SO_4, depending upon which reagent is preferred for the dehydration of SiO_2. If there is any evidence of incomplete decomposition of the sample after either wet or fusion attack, much trouble can be avoided by filtering off the insoluble matter, igniting, fusing with $K_2S_2O_7$ or $Na_2S_2O_7$, and dissolving the melt in the original solution before proceeding with the analysis.

(*c*) SILICA.—Two dehydrations with HCl or H_2SO_4 are sufficient in routine work. If HCl is used, the temperature of dehydration should not exceed 105 to 110° C. on account of the formation of insoluble aluminum compounds. If H_2SO_4 is used, a liberal excess must be present to keep the dehydrated mass from forming a solid cake which renders subsequent solution of the salts most difficult.

The first SiO_2 recovered must be very thoroughly washed with hot dilute HCl (5:95)[4] and then with hot water to remove salts of aluminum and the alkalies. The smaller second recovery is washed with cool dilute HCl (1:99) and then with hot water. The temperature at which SiO_2 is finally heated must not be less than 1,200° C., and the heating must be continued until constant weight is obtained. As the ignited oxide is somewhat hygroscopic, the crucible should be covered with a well-fitting cover during cooling and weighing, and the desiccator should contain a strong desiccant.

In analyses of the highest accuracy the SiO_2 that escapes two dehydrations must be recovered in the second filtrate by precipitating with NH_4OH, dissolving the precipitate in dilute H_2SO_4, evaporating to fumes of H_2SO_4, diluting and filtering. Less accurate, because of the solvent action of $KHSO_4$ or $NaHSO_4$, but satisfactory for most purposes, is the recovery based on the fusion of the weighed oxides as under the umpire method. The amount that is recovered varies. In analyses of a series of refractories with SiO_2 content ranging from 20 to 60 per cent the recoveries averaged 0.2 per cent in either HCl or H_2SO_4 dehydration. It is not safe, however, to arbitrarily add this amount of SiO_2, because in some cases as little

[3] If $Na_2B_4O_7$ is used, it must be removed before determinations of SiO_2 or Al_2O_3 are attempted, for otherwise part of the boron is carried down by SiO_2 and volatilized as the fluoride, BF_3, while part is carried down by the NH_4OH precipitate in spite of reprecipitations. Boron can be removed as follows: Place the melt in a large porcelain or platinum dish, cover and treat with a saturated solution of HCl in CH_3OH (prepared by passing dry HCl gas into cooled CH_3OH for one to two hours). When effervescence ceases, remove the cover and heat just short of boiling, preferably on a water bath in a good hood. Cleanse the crucible in a similar manner and add its contents to the dish. Add more reagent as necessary until solution is complete, boil to a small volume and evaporate to dryness on the bath. To remove the last traces of boron, evaporate to dryness at 80 to 85° C. on the bath two or three times with successive additions of small portions of the reagent, taking care to wash down the sides of the dish.

[4] Prepared by mixing 5 ml of HCl sp. gr. 1.19, with 95 ml of water. This system of designating dilute acids is used throughout the paper. For example, dilute H_2SO_4 (1:1), denotes a solution containing 50 ml of H_2SO_4, sp. gr. 1.84, and 50 ml of water.

as 0.04 per cent was recovered while in others the recovery amounted to 0.3 per cent.

(*d*) ALUMINA.—The chief sources of error in a determination of Al_2O_3 in bauxite or refractories high in Al_2O_3 are:

1. Failure to completely decompose the material. Whenever there is doubt as to the completeness of decomposition, the residue left after dissolving the melt should be fused, dissolved, and added to the original solution.

2. Failure to fuse the nonvolatile residue left after the treatment of the SiO_2 with HF and H_2SO_4. This residue must be fused, the melt dissolved, and the solution added to the filtrate from the SiO_2.

3. Failure to correct for all of the compounds that are normally carried down in the NH_4OH precipitate and weighed with the Al_2O_3. The following list of such compounds that are contained in the Bureau of Standards sample of bauxite No. 69 illustrates the extent of the errors that may be made if any or all of such corrections are omitted: Fe_2O_3, 5.66 per cent; TiO_2, 3.07 per cent; ZrO_2, 0.08 per cent; P_2O_5, 0.11 per cent; V_2O_3, 0.03 per cent; and Cr_2O_3, 0.04 per cent.

4. Failure to remove the alkali salts carried down by the NH_4OH precipitate. For example, after fusion of 0.5 g of bauxite with 7 to 10 g of Na_2CO_3 and elimination of SiO_2, the alkali salts in the ignited mixed oxides as determined by the J. Lawrence Smith method amounted to 0.7 mg after careful double precipitation and 0.1 mg after triple precipitation by NH_4OH. The error caused by the retention of alkalies may, therefore, be as high as 0.14 per cent of Al_2O_3 (on a 0.5 g sample) in spite of double precipitations and will be much greater if only a single precipitation is made.

5. Improper ignition of the NH_4OH precipitate. Blum [5] has shown that Al_2O_3 which has been heated over the blast lamp to constant weight undergoes no further loss upon heating to 1,440 to 1,460° C. As a result of his tests he states that ignition for 5 to 10 minutes over a blast lamp is sufficient to bring Al_2O_3 to constant weight. This statement is correct for small precipitates obtained from pure solutions. In ignitions of the large mixed precipitate obtained from bauxite or refractories the analyst must be sure that he is igniting at at least 1,200° C. and that constant weight has been obtained. For example, a precipitate containing 0.35 g of Al_2O_3 lost but 0.1 mg when heated in a muffle for one hour at 900° C. after a preliminary heating for a like period at 800° C. When heated for one hour at 1,050° C., it lost 1.4 mg, and upon heating over the blast it lost 1.5 mg more, both corrected for the loss of weight of the platinum crucible. The error caused by the retention

[5] B. S. Sci. Paper No. 286; J. Am. Chem. Soc., 38, p. 1282; 1916.

of water would therefore, have been 0.58 per cent of Al_2O_3 (on a 0.5 g sample) if heating had been stopped at 900° C. and 0.30 per cent if it had been stopped at 1,050° C.

6. Failure to protect the ignited residue from moisture before or during weighing. Ignited Al_2O_3 absorbs water readily and takes up in the first few minutes a large proportion of the water that it will absorb in 24 hours. This is important, as the atmosphere in a desiccator immediately after opening is not much different from that of the room. Fortunately, the rate of absorption is very slow if the crucible is covered with a well-fitting lid during cooling and weighing, and errors are negligible if a good desiccant is used in the desiccator and weighings are made rapidly. For example, a well-covered crucible containing 0.1 g of ignited Al_2O_3 showed no appreciable change in weight in five minutes on the balance pan but gained 1 mg in five minutes when uncovered. An oxide ignited at 1,200° C. is less hygroscopic than one ignited at 1,000° C.

7. Failure to correct for SiO_2 carried down by the NH_4OH precipitate. SiO_2 is always carried down by the NH_4OH precipitate, and the amount depends on the completeness of the recovery of SiO_2 at the start of the analysis and the amount afterwards introduced with the reagents, chiefly through NH_4OH. SiO_2 is always left in solution, even after double dehydration with HCl or H_2SO_4. In careful analyses the amount (on a 0.5 g sample) may represent as little as 0.05 per cent of Al_2O_3 and as much as 0.3 per cent.

8. Misleading corrections for impurities derived from the reagents or through attack on the vessels used. The small precipitate obtained by precipitation with NH_4OH in a solution of reagents alone does not, as a rule, carry down impurities, such as SiO_2 or P_2O_5, introduced through the reagents or during the analysis, as completely as does the much larger precipitate obtained from the material under analysis. For example, in analyses of 0.5 g portions of bauxite, an average correction of 0.25 mg was indicated by the reagents alone, 1.8 mg when 0.25 g of Al_2O_3 as pure $AlCl_3$ was added to the reagents and no correction for SiO_2 was made, and 0.9 mg when $AlCl_3$ was added and correction for SiO_2 was made. If the correction was based on reagents alone, the result for Al_2O_3 in the bauxite would, therefore, be high and differ by 0.13 from the true percentage. On the other hand, if no correction was made for the SiO_2 carried down by the added Al_2O_3 the result would be low and differ by 0.18 per cent from the true value.

2. UMPIRE METHOD FOR THE ANALYSIS OF BAUXITE OR REFRACTORIES OF HIGH ALUMINA CONTENT

(*a*) DRYING.—Transfer a portion of the sample to a weighing bottle of such diameter that the layer of sample is not more than one-half

centimeter deep. Dry bauxite for two hours at 140° C. and burnt refractories for one hour at 105 to 110° C. Cool over a good desiccant. In the most accurate analyses of bauxite each portion taken for analysis should be separately dried and the weight obtained by stoppering the bottle, cooling in a desiccator, lifting the cover for an instant, weighing, pouring out as much of the powder as possible without brushing, and again weighing.

(*b*) SOLUTION OF THE SAMPLE.—Thoroughly mix 0.5000 g of the dried sample with 7 to 8 g of Na_2CO_3 in a platinum crucible and cover the mixture with an additional gram of Na_2CO_3. Gradually, particularly with bauxite, heat the covered crucible and its contents until the mass is molten. After the mass is molten and the fusion is quiet grasp the crucible with a pair of tongs, slightly tilt and rotate it, so as to decompose particles which cling to the sides of the crucible above the molten mass. Finally heat at 1,000 to 1,100° C. for one hour. Cool and dissolve the melt in a platinum dish in 150 ml of dilute H_2SO_4 (1 : 9). If there is any indication of incomplete decomposition, filter the solution, wash the residue, and ignite the paper in the crucible used for the fusion. Fuse the residue with a small amount of Na_2CO_3 and add the cooled melt to the original solution.

If SiO_2 is not to be determined, bauxite can be almost entirely decomposed by the use of HF, HNO_3, and H_2SO_4 as described in the routine method. Burnt refractories are only partially decomposed by such treatment.

(*c*) DETERMINATION OF SILICA.—Evaporate the solution until fumes of H_2SO_4 appear, cool, and take up in 200 ml of water. Heat until the salts are in solution, and immediately filter through a No. 40 Whatman or similar paper. Wash very thoroughly with warm dilute HCl (5 : 95) and finally with hot water. It is very important that the SiO_2 be washed free from sodium salts. Reserve the paper and residue. Again evaporate the filtrate until fumes of H_2SO_4 appear and treat as before except that the residue should be washed with cool dilute HCl (1 : 99) instead of with the hot 5 : 95 acid. Reserve the filtrate (A). Char the two papers containing the SiO_2 in a platinum crucible, burn the carbon at as low a temperature as possible, and finally heat at approximately 1,200° C. Cool over a good desiccant and weigh. The heating should be very gentle at first to avoid mechanical loss of very finely powered SiO_2, and the crucible must be tightly covered during the final heating. If a blast lamp is used, the crucible should be set to two-thirds of its depth in an asbestos shield.

After constant weight has been attained carefully moisten the SiO_2 in the crucible and add a few drops of H_2SO_4 (1 : 1) and approximately 10 ml of HF. Evaporate, carefully expel the H_2SO_4, and again ignite to constant weight. The difference between the two

weights is SiO_2. To this must be added the SiO_2 recovered from the mixed oxides.

(*d*) DETERMINATION OF THE MIXED OXIDES.—Fuse the nonvolatile residue from the SiO_2 with a small quantity of $K_2S_2O_7$, cool, take up the melt in dilute H_2SO_4 (1:9), and add the solution to the filtrate from the determination of SiO_2 (A). Dilute this solution to 350 ml, add a few drops of methyl red indicator, heat to boiling and add NH_4OH until the red color just changes to a light yellow. Boil for one to three minutes and, if the red color of the indicator reappears, discharge it by adding another drop of NH_4OH. Filter through a No. 40 Whatman or similar paper and wash the precipitate 5 to 10 times with a hot neutral 2 per cent solution of NH_4Cl. Return the precipitate to the beaker in which the precipitation was made by washing it off the paper with a strong jet of water and dissolve it in 50 ml of hot dilute HCl (1:1). When the precipitate has dissolved, dilute to 350 to 400 ml, add the paper, stir until pulped, and repeat the precipitation and washing as before. Do not allow the precipitate to run dry on the filter, but keep the paper filled or nearly filled with wash solution. At least 250 ml of solution should be used in the final washing. If the precipitate is too large to go into the crucible, dry the paper and contents at 100 to 110° C. and then transfer to a platinum crucible that has been weighed with cover. Ignite at a low temperature and under good oxidizing conditions at first and finally cover and heat at approximately 1,200° C. Cool over a good desiccant, never $CaCl_2$, and weigh quickly. Repeat the heating and weighing until constant weight is obtained. The precipitate contains the Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, V_2O_5, Cr_2O_3[6] which were present in the sample, besides the SiO_2 which escaped the double dehydration.

In order to arrive at the true weight of Al_2O_3, it is necessary to determine the weights of the other substances as described below and to subtract from the total weight. As the quantities of the accompanying substances are relatively small, this method of obtaining Al_2O_3 (by difference) yields results that are quite acceptable, although an accuracy better than 1 part in 200 can hardly be expected.

(*e*) RECOVERY OF SILICA.—Fuse the mixed oxides with $K_2S_2O_7$, cool, and dissolve the melt in 100 ml of dilute H_2SO_4 (1:9). Evaporate to incipient fumes of H_2SO_4, cool, add 150 to 200 ml of warm water, heat until the salts are in solution, and immediately filter and wash the small amount of SiO_2. Reserve the filtrate (B). Ignite, weigh, treat with HF and H_2SO_4 as previously described, and again weigh. Add this SiO_2 to that previously obtained. Fuse the small

[6] Cr_2O_3 by itself is partially oxidized during ignition and is no doubt partly oxidized during the ignition of the mixed oxides. If the total amount involved is small, as in the usual case, no appreciable error is caused if calculations are based on the oxide, Cr_2O_3. If large amounts of chromium are present, as in chrome brick, accurate results can only be obtained by determining the chromium (preferably by volumetric titration) in a separate portion of sample and oxidizing it to the chromate before the mixed oxides are precipitated.

nonvolatile residue with a little $K_2S_2O_7$, dissolve the melt in dilute H_2SO_4, and add to the reserved filtrate (B).

(*f*) DETERMINATION OF P_2O_5, Cr_2O_3, AND V_2O_5.—Nearly neutralize the combined filtrates (B) with NaOH and pour the solution (not over 100 ml in volume) slowly and with constant stirring into 150 ml of a 10 per cent solution of NaOH containing 1.0 g of Na_2O_2. Digest on the steam bath for 1 hour to oxidize the chromium to chromate and to decompose the excess of peroxide, cool, and filter through a paper which has been treated with NaOH of the same strength. This treatment of the paper will prevent the extraction of coloring matter from the paper. Wash the precipitate with hot water and reserve it for the determination of Fe_2O_3, TiO_2, and ZrO_2 (C). Determine the chromium in the filtrate colorimetrically by comparing the color with that obtained by adding a standard solution of chromate to an alkaline solution of the same strength.

After the color comparison acidify the solution and add a very slight excess of NH_4OH in order to precipitate the aluminum which will also carry down any phosphorus and vanadium present. Do not use an indicator such as methyl red in this precipitation, as its color may subsequently interfere with the determination of vanadium. Litmus is sufficiently sensitive, as phosphorus and vanadium will not be lost unless a large excess of NH_4OH is added. The precipitation with NH_4OH at this point is introduced to get rid of the Na_2SO_4 which would otherwise interfere with the precipitation of phosphorus. Incidentally, the most of any chromium and of elements such as platinum and molybdenum are also removed. Filter, dissolve the precipitate in 100 ml of dilute HNO_3 (1:9), and add a few drops of H_2O_2. If any color develops, compare with a standard solution of vanadium under the same conditions.

After the vanadium has thus been determined colorimetrically, transfer the solution to a 300 ml Erlenmeyer flask and destroy the H_2O_2 by boiling vigorously for one or two minutes and then adding a saturated solution of $KMnO_4$ dropwise until a pink color persists. Decolorize by the addition of a few drops of H_2SO_3, add 15 ml of HNO_3 (sp. gr. 1.42), cool, adjust the volume to about 125 ml, and add 40 ml of dilute NH_4OH (sp. gr. 0.96) and 40 ml of molybdate reagent.[7] Shake for 10 minutes, allow to stand for one-half hour, filter and wash the flask, paper, and precipitate 10 times with a 1 per cent solution of KNO_3. Return the precipitate and paper to the precipitating flask, add an excess of standard 0.1 *N* NaOH and 25 ml of water (both free from CO_2), and shake until the precipitate is dissolved. Dilute to 100 ml, add three drops of a 0.2 per cent

[7] For the preparation of this reagent mix 100 g of pure MoO_3 or 118 g of 85 per cent molybdic acid with 400 ml of water and add 80 ml of NH_4OH (sp. gr. 0.90). When solution is complete, filter and pour the solution slowly and with constant stirring into a mixture of 400 ml of HNO_3 (sp. gr. 1.42) and 600 ml of water. Let settle for 24 hours and use the clear supernatant liquid.

solution of phenolphthalein, and discharge the pink color with standard acid. Finish the titration by adding standard alkali until the pink color reappears. The alkali solution is preferably standardized against the Bureau of Standards acid potassium phthalate or benzoic acid, and the ratio of P_2O_5 to NaOH should be considered as 1:46 in calculating results.

If it is preferred, the phosphorus may be determined gravimetrically by solution of the phosphomolybdate and double precipitation by magnesia mixture.[8]

As the reagents may contain phosphorus, a careful blank carried through all steps of the determination is essential. It is desirable that a known amount of aluminum corresponding to that in the regular analysis be added to the blank. If aluminum is not added, the most if not all of the phosphorus in the reagents would be lost in the precipitation with NH_4OH, while in the regular determination it would be carried down by the aluminum present in the sample. The results for phosphorus would then be correspondingly high.

(*g*) DETERMINATION OF Fe_2O_3, TiO_2, AND $ZrO_2(HfO_2)$.—Dissolve the reserved precipitate (C) in 25 ml of hot dilute HCl (1:2), add 4 g of tartaric acid, dilute with water to a volume of 200 ml, and neutralize with NH_4OH. Add 2 ml of HCl per 100 ml of solution, heat to boiling, and saturate with H_2S. Allow to cool and filter off any platinum sulphide which may have separated and wash with a 1 per cent solution of H_2SO_4 saturated with H_2S. Render the filtrate slightly ammoniacal, pass in a rapid stream of H_2S for five minutes, and digest at the side of the steam bath (40° C.) 15 to 30 minutes. Filter and wash with a dilute solution of $(NH_4)_2S$ (5:95) containing 5 g of NH_4Cl per liter. Reserve the filtrate (D).

Dissolve the iron sulphide in hot dilute HCl (1:1) to which has been added a little $KClO_3$, evaporate to dryness, take up in 25 ml of dilute HCl (5:95), and add $KMnO_4$ until the usual pink color is obtained. Reduce with $SnCl_2$ and titrate slowly with a standard solution of $KMnO_4$, as in the Zimmermann-Reinhardt method.

The filtrate (D) contains the titanium and zirconium. Acidify this solution with H_2SO_4, dilute to 200 ml, adjust the acidity so that the solution contains 10 ml of H_2SO_4, sp. gr. 1.84 per 100 ml, and cool in ice water. It is unnecessary to destroy tartaric acid. Precipitate the titanium and zirconium with an excess of a cold 6 per cent water solution of cupferron.[9] An excess of the precipitant is indicated by the formation of a fine white precipitate which redissolves, instead of a curdy one which persists. Stir in a little macerated paper, allow to settle for five minutes, filter by suction through

[8] G. E. F. Lundell and J. I. Hoffman, Ind. Eng. Chem., **15**, pp. 44 and 171; 1923.

[9] O. Baudisch, Chem. Ztg., **33**, p. 1298; 1909; W. M. Thornton, jr., Am. J. Sci. (4), **37**, pp. 173, 407; 1914; W. M. Thornton, jr., and E. M. Hayden, jr., ibid. (4), **38**, p. 137; 1914; G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc., **42**, p. 1439; 1920.

a paper and cone, and test the filtrate for complete precipitation. Thoroughly wash the precipitate with cold dilute HCl (1:9). Transfer to a weighed platinum crucible, carefully dry, then cautiously char and burn the carbon, and finally heat at approximately 1,200° C. over a blast lamp or its equivalent. Cool in a desiccator, weigh as ZrO_2+TiO_2, and repeat the ignition until constant weight is obtained. The correction of the weighed oxides for SiO_2 by direct treatment with H_2SO_4 and HF is a difficult procedure and is well-nigh impossible if the residue is large. The amount of SiO_2 is usually small and can be determined if desired by evaporating the H_2SO_4 solution of the pyrosulphate melt obtained in the next step to fumes of H_2SO_4, diluting so that the solution contains 10 per cent of the acid by volume, and recovering the SiO_2 by filtering and washing.

Fuse the precipitate of TiO_2 and ZrO_2 with a small amount of $K_2S_2O_7$, dissolve the melt in 50 ml of dilute H_2SO_4 (1:9), add sufficient H_2O_2 to oxidize all of the titanium (an excess does no harm), add 0.5 g of $(NH_4)_2HPO_4$, allow to stand at the side of the steam bath (40° C.) overnight, filter, wash with a 5 per cent solution of NH_4NO_3, ignite and weigh as ZrP_2O_7. Calculate to ZrO_2 and subtract from the total weight of TiO_2+ZrO_2. As a check, titanium can be determined colorimetrically, before the precipitation of zirconium. In very accurate analyses the ZrP_2O_7 should be fused with a little $K_2S_2O_7$, the melt dissolved in 10 per cent H_2SO_4 as before, and the precipitation repeated. More phosphate must be added in the second precipitation, and an excess of H_2O_2 should be present at all times.

(*h*) Determination of Lime and Magnesia.—For the determinations of CaO and MgO a new and larger sample (1–5 g according to the quantity of CaO and MgO expected) should be used. Put the sample into solution by fusing with Na_2CO_3 or treating with HF, HNO_3, and H_2SO_4, as directed under "Solution of the sample." If the solution of the sample is accomplished by fusion with Na_2CO_3, SiO_2 must be eliminated. Nearly neutralize the SiO_2-free solution with NaOH, dilute to 100 ml, and pour slowly and with constant stirring into 150 ml of a 10 per cent solution of NaOH containing 1.0 g of Na_2CO_3. If the sample does not contain iron, it is advisable to make sure of complete precipitation of titanium and to aid the agglomeration of calcium and magnesium by adding about 0.01 g of iron as $FeCl_3$ to the solution of the sample before pouring it into the NaOH–Na_2CO_3 solution. Digest on the steam bath for one-half hour, allow to cool, filter, and wash a few times with a 1 per cent solution of Na_2CO_3.

Dissolve the precipitate in 25 ml of hot dilute HCl (1:2), and in this solution precipitate the iron, titanium, etc., by addition of a slight excess of NH_4OH, using methyl red as indicator. Filter,

dissolve the precipitate, and repeat the precipitation with NH_4OH. If it seems desirable to determine iron (provided no iron was added) titanium, and zirconium on a large sample, the precipitate obtained here may be dissolved in HCl and the iron, titanium, and zirconium determined as previously described. In the combined filtrates precipitate the calcium as oxalate in slightly ammoniacal solution, filter, and wash with a cold 1 per cent solution of $(NH_4)_2C_2O_4$.

Dissolve the precipitate in a small amount of hot dilute HCl and repeat the precipitation of calcium in a volume of 50 ml. Filter, wash as before, ignite, and weigh as CaO.

Combine the filtrates from the calcium determination, acidify with HCl, and precipitate the magnesium by adding 2 g of $(NH_4)_2HPO_4$ to the cold acid solution, then NH_4OH slowly and with stirring until the solution is just alkaline and finally 10 ml in excess. Allow the solution to stand for at least 12 hours, filter, dissolve the precipitate in dilute HCl, and repeat the precipitation in a volume of 50 ml. A few crystals of $(NH_4)_2HPO_4$ should be added to the acid solution before the second precipitation. Dry the paper and precipitate in a weighed crucible, char without inflaming, burn the carbon at a temperature below 700° C., and finally heat at 1,000° to 1,100° C. Cool in a desiccator and weigh as $Mg_2P_2O_7$.

(*i*) DETERMINATION OF THE ALKALIES.—Alkalies can be satisfactorily determined by the J. Lawrence Smith method.

3. ROUTINE METHOD FOR THE DETERMINATION OF ALUMINA IN BAUXITE OR REFRACTORIES OF HIGH ALUMINA CONTENT

Transfer 2.000 g of the dried sample to a platinum dish and add 25 ml of water, 15 ml of concentrated H_2SO_4, 25 ml of concentrated HNO_3, and about 20 ml of HF. Cover the dish with a platinum cover and digest on the steam bath for 15 to 30 minutes with occasional stirring. Remove the cover, place the dish over a low flame, and evaporate to copious fumes of H_2SO_4. Cool, thoroughly wash the inside surface of the dish with a jet of water, mix the contents of the dish thoroughly, and again place over the flame. Heat to incipient fumes of H_2SO_4, cool, add 50 ml of warm water, and heat until the salts are in solution. If the solution is not entirely clear, add a little macerated paper, filter, wash with hot water, and reserve the filtrate (A). Ignite the paper and residue in a platinum crucible and fuse with the minimum quantity of Na_2CO_3. Cool the melt and dissolve it in an excess of dilute H_2SO_4.

If the ignited insoluble residue was small (less than 1 to 2 mg), add the solution of the melt directly to the reserved filtrate (A). If the ignited insoluble residue was large, as is usually the case with high

[1] "For example, approximately 15 per cent of the sample was undissolved in tests of a refractory containing 32.38 per cent of SiO_2 and 59.39 per cent of Al_2O_3.

alumina refractories,[10] it may contain some SiO_2. In this case add HF and evaporate the solution to incipient fumes of H_2SO_4. Cool, wash down the sides of the dish, and evaporate as before. Cool, add 50 ml of warm water, and add the solution to the reserved filtrate (A).

When the sample is completely dissolved, cool, transfer it to a 500 ml graduated flask, dilute to the mark, mix, and remove with a pipette (1) a 100 ml portion for precipitation by NH_4OH, (2) a 100 ml portion for precipitation by cupferron, and (3) a 200 or 250 ml portion for the determination of P_2O_5. (If the percentage of P_2O_5 is low, it is advisable to take as large an aliquot as possible.)

(*a*) PRECIPITATION BY AMMONIUM HYDROXIDE.—Dilute the first aliquot to 350 ml, add a few drops of methyl red indicator, and proceed as in the umpire method, but make only one precipitation by NH_4OH. The weighed precipitate will contain the Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, V_2O_5, and more or less of the Cr_2O_3[11] which were present in the sample.

(*b*) PRECIPITATION OF Fe_2O_3, TiO_2, ETC., BY CUPFERRON.—Neutralize the second aliquot with NH_4OH, add 40 ml of dilute, H_2SO_4 (1:1), dilute to 200 ml, and cool in ice water. Precipitate with an excess of a cold 6 per cent water solution of cupferron, filter, wash, ignite, and weigh as in the umpire method for TiO_2 and ZrO_2. The weighed residue contains the Fe_2O_3, TiO_2, ZrO_2, and V_2O_5 which were present in the sample. Subtract this weight from that of the NH_4OH precipitate to obtain the weight of the $Al_2O_3+P_2O_5+Cr_2O_3$ in a 0.4000 g sample.

(*c*) DETERMINATION OF P_2O_5.—Nearly neutralize the third aliquot with NaOH and pour it slowly and with constant stirring into 100 ml of a 10 per cent solution of NaOH. Allow the precipitate to settle, filter, and wash a few times with a 1 per cent solution of NaOH. Acidify the filtrate with HNO_3, and precipitate the aluminum and phosphorous by the addition of a slight excess of NH_4OH.[12] Filter wash the precipitate a few times with a 2 per cent solution of NH_4NO_3. By the use of a spatula transfer the bulk of the precipitate from the paper to the beaker in which the precipitation was made, add 100 ml of dilute HNO_3 (sp. gr. 1.135), heat and digest until the precipitate is dissolved. Pour this solution through the paper to remove any remaining precipitate and catch the clear solution in a 300 ml Erlenmeyer flask. Cool the solution to room temperature, add 40 ml of dilute NH_4OH (sp. gr. 0.96) and 40 ml of molybdate reagent, shake

[11] The proportion of the original chromium that is caught in the NH_4OH precipitate is a matter of doubt because of possible oxidation during solution of the sample. Moreover, partial oxidation of the oxide Cr_2O_3 may occur during ignition. Fortunately, so little chromium is usually present in the original material that it can be ignored. In the exceptional case it is best to make sure of its complete oxidation to the sexivalent state during solution of the sample.

[12] The precipitation of phosphorus as ammonium phosphomolybdate is slow or incomplete in the presence of titanium or of large quantities of Na_2SO_4. Titanium is removed by the first and sodium salts by the second treatment.

for 10 minutes, allow to stand for one-half hour, and proceed as described in the umpire method. Calculate the percentage of P_2O_5 in the sample and subtract from the percentage of $Al_2O_3 + P_2O_5 + Cr_2O_3$, found above.

The routine method can be used as an umpire method if the following refinements are added: (1) Repeat the precipitation with NH_4OH and correct the ignited and weighed precipitate for SiO_2; (2) carefully ignite the cupferron precipitate at a low temperature, fuse it with $K_2S_2O_7$, and repeat the precipitation with cupferron.

If a more complete analysis is desired, the precipitate obtained by NaOH preliminary to the determination of phosphorous can be analyzed for Fe_2O_3, TiO_2, ZrO_2, etc.

Three analyses of the Bureau of Standards standard sample of bauxite No. 69 by the routine method gave 55.02, 55.22, and 54.76 per cent of Al_2O_3 as against the certificate value of 55.06.[13] A single run in which the NH_4OH and cupferron precipitations were repeated gave 54.92. Two analyses of the bureau's burnt refractory No. 77 gave 59.40 and 59.60 per cent of Al_2O_3 by the routine method as against the certificate value of 59.39 per cent.[14] Double precipitations by NH_4OH and cupferron gave 59.18 and 59.38 per cent.

[13] This sample also contains 5.66 per cent of Fe_2O_3, 3.07 per cent of TiO_2, 0.08 per cent of ZrO_2, 0.11 per cent of P_2O_5, 0.03 per cent of V_2O_3, and 0.04 per cent of Cr_2O_3.

[14] This sample also contains 0.90 per cent of Fe_2O_3, 2.93 per cent of TiO_2, 0.09 per cent of ZrO_2, 0.45 per cent of P_2O_5, and 0.032 per cent of V_2O_5.

WASHINGTON, October 31, 1927.

Announcement

Bureau of Standards Journal of Research

Beginning July, 1928, a new periodical to be known as the

"Bureau of Standards Journal of Research"

supersedes and continues the two series of research publications heretofore issued under the designations "Scientific Papers of the Bureau of Standards," and "Technologic Papers of the Bureau of Standards."

Forty-four volumes of the two superseded series have been published. The 22 volumes of scientific papers issued by the bureau (since 1904) contain some 572 research papers on fundamental science, and the 22 volumes of technologic papers (issued since 1910) contain some 370 research papers on applied science.

The new Bureau of Standards Journal of Research will publish the results of the bureau's researches (both theoretical and experimental). It is expected the monthly issues will range from 100 to 300 pages, an average issue containing about 200 pages. Subscriptions ($2.75 per year, United States, Canada, and Mexico) should be placed direct with the "Superintendent of Documents, Government Printing Office, Washington, D. C." ($3.50 for foreign subscriptions.)

Shortly after each month's Journal is published, reprints of the separate articles contained may be purchased from the Superintendent of Documents.